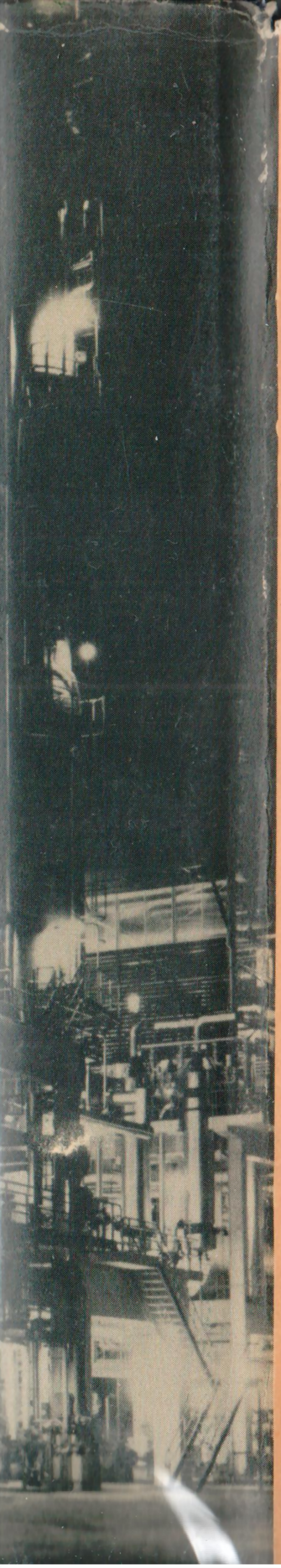

WADDAMS Chemicals from PETROLEUM

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Chemicals from PETROLEUM

A. L. WADDAMS

Chemicals from PETROLEUM

A large and vitally important section of the world's chemical industry is based on petroleum. This is a development which has taken place with astonishing speed during the past quarter of a century, and especially in the last ten years. Many of the products serve the vastly growing needs of industrial processing, and therefore remain unknown to the general public, but the impact of such products in the case of plastics, detergents and synthetic fibres has caught widespread public attention.

Yet there is only a handful of books on the subject of chemicals from petroleum, and there is no recent book that emphasises the subject from the point of view of the products and processes of major industrial importance.

This book attempts to fill this enormous gap. Its author has been able to draw on wide experience with the Shell group of companies in Britain, Europe, the U.S.A. and Australia. The chapters of the book are divided into three sections:

(i) Background, in which the characteristics of this industrial field and the raw materials are discussed;

(ii) Details of petroleum chemical processes, products and applications; and

(iii) The industrial pattern.

This final section gives a picture, backed by statistics, of the vast number of uses to which these chemicals are now being put and of the prospects for the future.

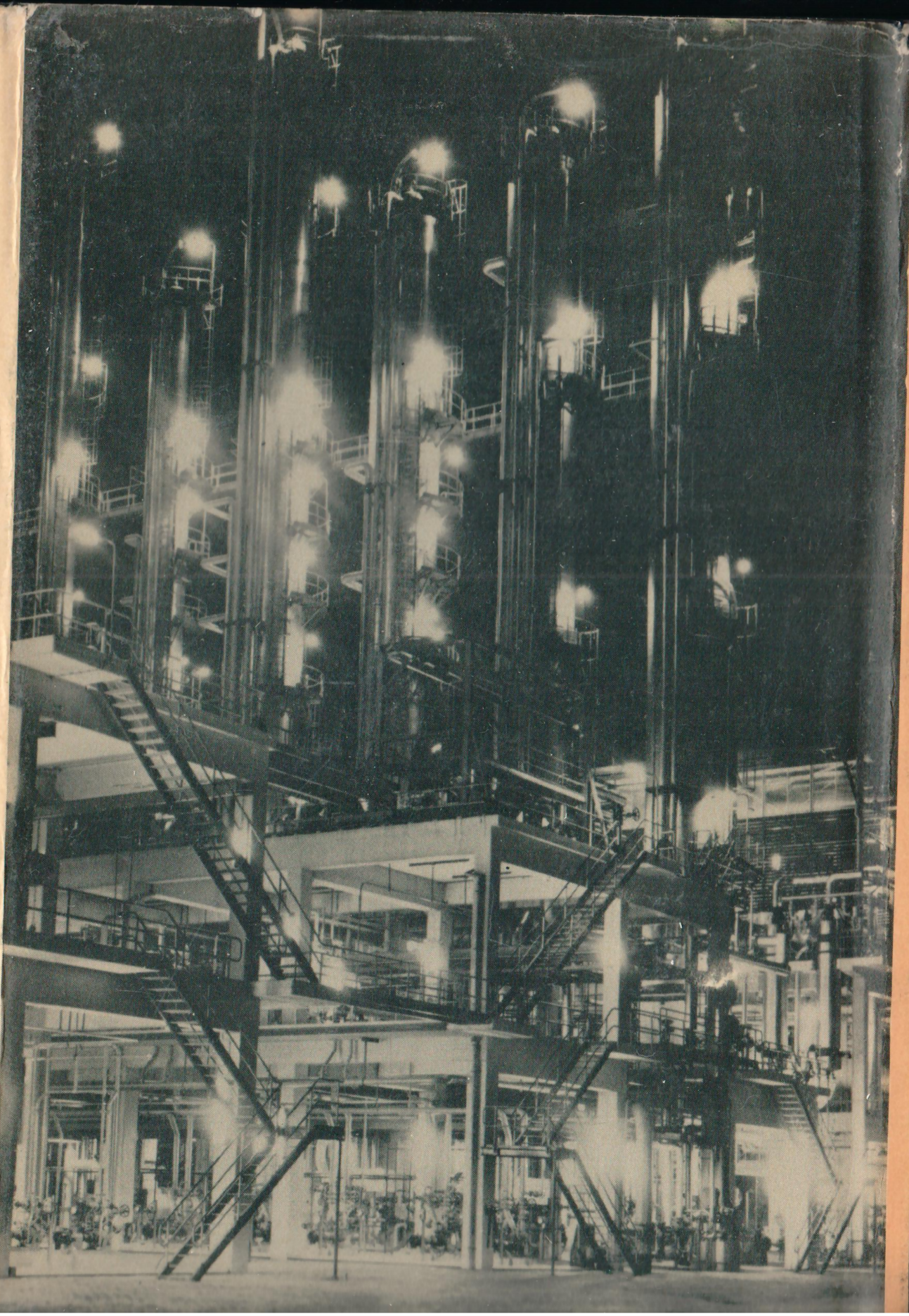
$6

Austen Lawrence Waddams was educated at Latymer Upper School in London, England and Imperial College, University of London. He graduated in chemistry and took advanced postgraduate work in chemical engineering.

Since 1945, Mr. Waddams has been associated with the petrochemical field in various companies of the Shell group in England as well as in Australia. During this period he has seen the petrochemical industry of the United Kingdom develop from negligible proportions to a major factor in the chemical industry.

He was a pioneer in petrochemical development in Australia and was closely associated with its first plant for producing chemicals from petroleum at Geelong, Victoria. From 1954 to 1960 he was Manager of the Projects and Services Division of Shell Chemical (Australia).

The author's experience has been widely diversified throughout the petrochemical field, making him unusually qualified to author a book of such wide scope.



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Acknowledgment

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Page 53 — Ethyl Alcohol from Ethylene flowsheet
Page 58 — Ethylene Oxide flowsheet
Page 80 — Isopropyl Alcohol flowsheet
Page 86 — Glycerine from Propylene flowsheet
Page 97 — Butadiene from Butylenes flowsheet
Page 110 — Ammonia from Natural Gas flowsheet
Page 134 — Carbon Black by Oil Furnace flowsheet

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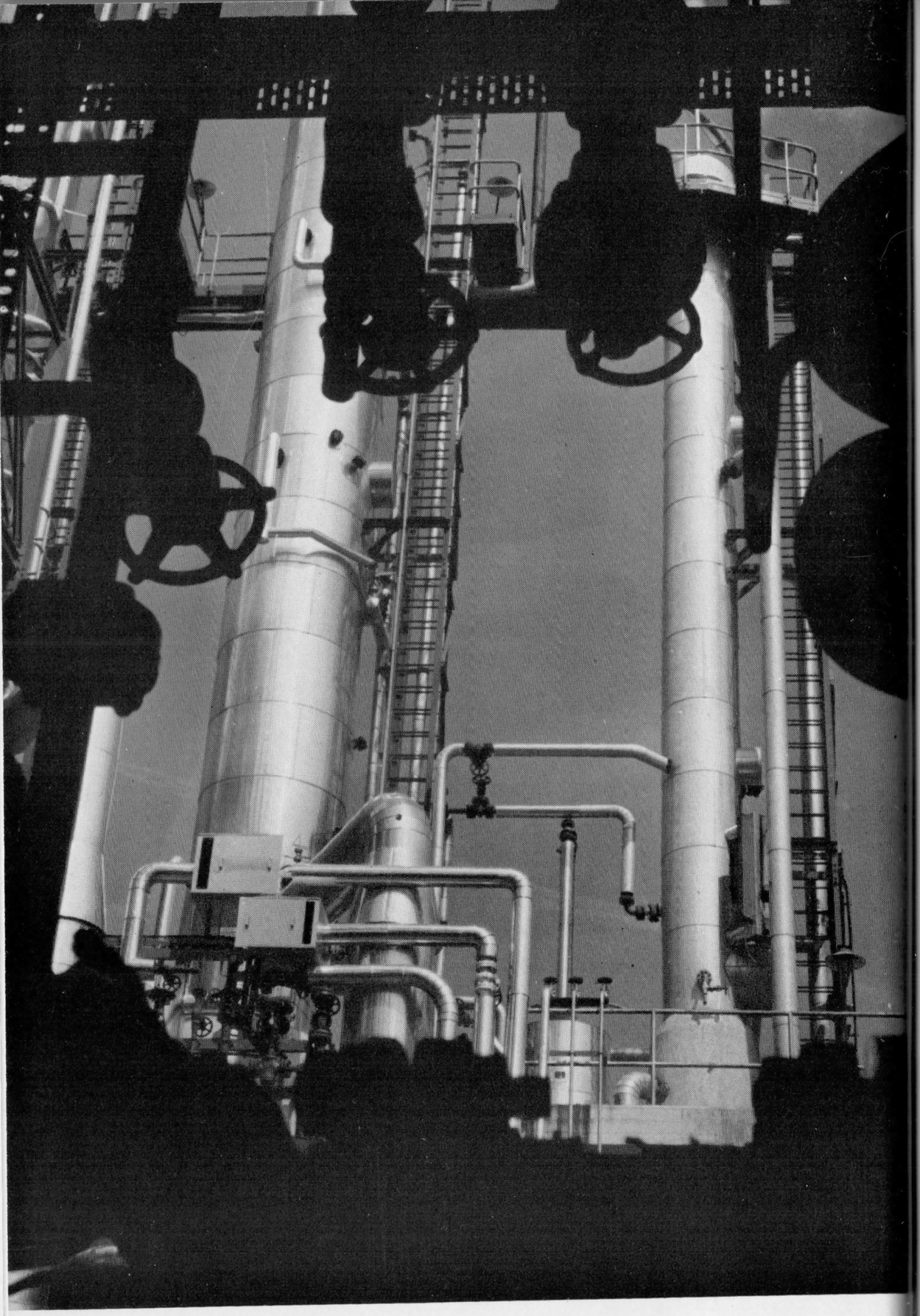
CHEMICALS FROM PETROLEUM



A striking photograph of a synthetic glycerine plant at Pernis, Holland

Courtesy Shell Nederland

CHEMICALS FROM PETROLEUM

an introductory survey

A. Lawrence Waddams

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Preface

This book is a concise technical account of an important sector of the chemical industry about which all too little is available elsewhere in book form. While it attempts, therefore, to give a clear yet accurate picture of the main chemical principles involved, the primary emphasis is on the structure and ramifications of the industry; and in view of this some brief observations on the economic background have also been included.

The limitations inherent in covering so large a subject within so brief a compass are obvious; the objective has been to draw attention to products and processes which are both industrially important and of technical significance in this particular field.

It may be desirable to direct the attention of academic readers to the minor limitations in accuracy of most commercial and some industrial statistics, a subject which is treated in more detail in the final chapter.

One of the fascinations of a study of chemicals from petroleum is its constant change. The text is an attempt to present the situation as it appeared at the end of 1961. There is little doubt that the scope of petroleum chemical production will change and enlarge during the early 1960's. Nor does our experience to date suggest that the more distant future will witness any slowing-down in this impressive advance.

In his task of extracting a coherent picture out of such kaleidoscopic movement, the author's labour has been much lightened by the willing collaboration of many colleagues in Shell Chemical Co. Ltd and other companies within the Shell group.

A. L. W.

July 1962

Part 1

Background to Petroleum Chemicals

Chapter 1

Introduction

The chemical industry is of ancient origin, and is founded on a wide variety of sources of raw materials. Amongst the most important historically of these have been coal, molasses, fats and oils (of vegetable and animal origin), salt, metalliferous ores, water and the atmosphere.

The appearance of petroleum as a significant source of chemicals (if we exclude the special case of carbon black) dates back only to the middle 1920's. The early development of chemicals from petroleum, for reasons discussed in the next chapter, took place almost exclusively in the U.S.A. This development has continued in the U.S.A. with practically no check until the present day, so that it is not surprising to find that today the production of chemicals from petroleum in the U.S.A. is far greater than that of the whole Western European complex, which is the next largest development. (Canada is a rather special case; she has received some stimulus from developments in the U.S.A., but the chronological development of her petroleum chemical production tends to follow the European pattern.)

Petroleum chemicals form part of the chemical industry, so that their substantial development can best be anticipated in areas with a highly developed chemical industry. The early limitation restricting development beyond the U.S.A. was the lack of availability of raw materials. Prior to 1939 it was the policy of the petroleum industry to locate refining capacity in close proximity to the source of the crude oil. After 1945 (for a variety of reasons, beyond the scope of this book to explore) it became the policy to locate oil-refining capacity in the regions of major consumption. This resulted in a vast expansion in the refining capacity of Western Europe, and caused attention to be diverted to the possibility of chemical production from these refinery resources. During the decade 1950–1960 the development of petroleum chemical production in Europe has been an outstanding feature even in a picture of widespread expansion of

industrial activity. The final chapter of this book provides the statistical picture of these developments.

Moreover, the use of petroleum as a basis for chemical production is now spreading to new areas. Japan and Australia already have substantial production at the operation or planning stages. The next few years will see many new plants in Latin America and a number of Asian countries. There are a number of plants projected for countries of the Middle East, and of Africa. The production of chemicals from petroleum is well on the way to being a world-wide development.

Since petroleum is essentially a mixture of hydrocarbons, the chemicals made from it are nearly all organic chemicals. They stray over into the inorganic field only for specific reasons. Carbon black and hydrogen cyanide are commonly classed as inorganic on an arbitrary basis. Sulphur is present as an undesirable impurity in certain crude oils, and may be recovered either as the element or as sulphuric acid. In ammonia production, it is the hydrogen which is required from petroleum. There is another special influence here, in that the carbon content of the petroleum may, in effect, be replaced by hydrogen by application of the shift reaction as outlined on page 107. These examples outline the limited range of inorganic chemicals which may commonly be derived from a petroleum source.

In theory virtually any organic chemical may be made from petroleum. In practice, whilst the range is wide, it is not unlimited. Other raw materials have a well-entrenched place in the organic chemical field, and in many cases such production is still expanding. This is certainly true of chemicals from coal in Europe. Fermentation chemicals, on the other hand, show some tendency to decline in several areas. The issue is generally one of economics. In many cases the same compound can be derived from more than one raw material. There will obviously be a tendency to use the most economic raw material. Such a trend is likely to be gradual, firstly because relative economic conditions will vary between one area and another, and secondly because production in an older plant has the advantage of lower fixed charges (for two reasons; one being the normal effect of inflation, and the second being the effect of plant depreciation allowances over a period of years). Moreover, there is a general rise in chemical production as a whole, so that even where a raw material may be losing ground relative to its competitors, it may

still retain its position, or even improve it, in terms of absolute tonnage.

The development of chemicals from petroleum has not, to a major degree, been at the expense of other raw materials, but rather complementary. Many of the chemicals made from petroleum have developed from negligible proportions to major industrial products within a period of 10–15 years.

The availability of a range of petroleum raw materials opened up a number of new horizons for the chemical industry. Some were economic, some chemical and some technological. The successful development of the opportunities thus created was a challenge both to the petroleum and chemical industries. This book records how that challenge has been met.

Chapter 2

Characteristics of Petroleum Chemical Manufacture

Petroleum chemical manufacture represents that segment of the chemical industry which is concerned to produce chemical products from raw materials of petroleum origin. Operating in this field are petroleum companies who have extended their interests into chemicals, chemical companies who buy in their petroleum raw materials, and joint ventures between chemical and petroleum companies, amongst many others (a very mixed bag, including plastics producers, textile companies, shipping companies and a sprinkling of governments). The manufacture of petroleum chemicals has therefore proved a meeting ground for the petroleum and chemical industries, introducing some features novel to each, and creating an entity with a character somewhat distinct from either of its parent industries.

Such differences should not be laboured, however, for there is no doubt that the rightful place for petroleum chemical production is solidly within the confines of the chemical industry.

The petroleum industry has its own cherished traditions. Above all else, it is big. A medium-sized refinery is likely to consume around five million tons of crude oil each year. The capacity of individual plant units is, therefore, huge by the standards of most industries, but will represent quite a modest proportion of the total market for the appropriate products in the market area serviced.

Almost all petroleum products can be handled in a fluid form. Refineries, therefore, present a spectacular array of pipe tracks and tank farms, for the handling of raw material and finished products. Petroleum technology is favourably influenced by this fact. Such advanced techniques, for example, as the fluid catalyst bed (in which control of the catalyst movement is exerted by the flow of the reactants) have been developed. The whole background, in short,

favours the development of large-scale, continuous, highly automated operations. High temperatures and catalytic promotion are frequently resorted to, but extremely high pressures and severe conditions of corrosion stress (such as are found in certain chemical manufactures) are uncommon.

Petroleum products are very rarely identifiable chemical compounds. They are more commonly prepared as blended products, required to meet a series of physical specifications, with occasional chemical interpolations as to impurities. This factor provides oil-refining operations with a significant degree of flexibility. Many of these blended products are prepared for markets whose standards of acceptance are well known and of long standing.

The phenomenon of the 'performance specification' is not unknown in the petroleum industry, but performance specifications for oil products are more commonly amenable to specific techniques of assessment operated within the refinery area (for example, the octane number of gasoline).

The chemical industry is rather more diverse. It ranges all the way from large-scale plants (still pretty small by petroleum standards, however), to small untidy batch-operated units, where, it appears, the spirit of alchemy sometimes still breathes. The chemical technologist has to face raw materials which include coal, salt, and metallic ores. The products are commonly pure compounds, with specifications governed by closely defined standards of chemical purity.

Petroleum chemical manufacture commonly requires the application of typically petroleum processing techniques to typically chemical finished products. Both the oil and the chemical partners in such enterprises found they had something to learn.

Petroleum chemical units are usually continuous, elaborate, operating with catalytic promotion, and highly automated. They consequently require a large scale of operation to secure an economic advantage. Unless there is an economic advantage, there is little purpose in the development of petroleum raw materials to serve the chemical industry in any particular instance. By their nature, petroleum chemical units are very subject to the consideration of 'minimum economic size', and it is necessary to digress for a moment to establish this point.

The question of plant size assumes economic significance in any

operation where the capital cost of the plant represents, in the form of depreciation, maintenance, etc., a substantial factor in the cost of the finished product. This situation is almost universally encountered in petroleum refining and petroleum chemical manufacture, but is slightly less common in some sections of the traditional chemical industry, where raw material costs may be of overwhelming importance. The economic importance of determining the most suitable plant capacity derives from the fact that the cost of building a plant is not proportional, in a simple sense, to the capacity (in practice, it is frequently assumed that the capital cost of plant will vary in proportion to the capacity taken to the power 0·6). The net effect of this expressed simply, is that building a plant of double capacity will not require double the cost. So long as the plant can be operated at its maximum capacity, it is clear that there is an economic incentive to design it on the largest possible scale. At the lower end of the capacity scale, the effect of depreciation increases by leaps and bounds. In a given set of conditions, therefore, which will reflect the facilities operated by competitive companies, it is important to ensure that any project envisaged includes production facilities of not less than 'minimum economic size'.

Having established the minimum economic size for a particular operation in a particular area, it is necessary to take a clear, cold look at the market available. A single petroleum chemical unit may be expected to serve a much higher proportion of the total market than most petroleum units would do. Since the final product is likely to be the subject of precise chemical specification, there is little flexibility in production available to such units. A new chemical product has to find its market either in competition with an accepted product, or in an entirely new field. The building of a plant of too great a capacity, therefore, will leave it under-occupied for an extended period. This factor may be accentuated, in the case of a new product, by the necessity to secure its full technical acceptance before market development can proceed.

The increasing movement of petroleum chemicals into the plastics field introduces some further novel and troublesome elements. The properties of plastics are rarely defined adequately in terms of chemical composition and such physical properties as melting point, viscosity, etc. Such items may well form part of the specification, but the ultimate requirement can only be expressed in terms of performance. Here, however, the 'performance specification' is a good deal more difficult to establish than is common in the field of petroleum. The customer requires the plastics he purchases to perform to his satisfaction, in his equipment, on his premises. The fabrication of plastics involves a multitude of small enterprises, calling forth much individual initiative and catering for a variety of specific individual requirements. Whilst this situation has permitted the dynamic growth of the industry as a whole, it also created the need for a very high standard of specialized technical service. This background of experience was entirely new to those brought up in the traditions of petroleum.

Just as the oil partners in the petroleum chemical complex had something to learn, the chemical partners have also secured some benefit from the association with techniques borrowed from the oil industry. One factor may be illustrated by reference to manpower statistics. Chemical production in the O.E.E.C. countries of Western Europe expanded 57 per cent between 1954 and 1959, whereas the labour force increased by only 13 per cent. A major factor in this respect has been the expansion of petroleum chemical production during this period, with its emphasis on automation, and hence on relatively low manpower requirements. (One must admit, on the other hand, that certain elements in the chemical industry, such as the production of fine chemicals, do not lend themselves to large-scale automated production units. Fine chemicals are more commonly produced in diverse, small-scale, versatile, batch-operated units.)

The specialized nature of the processes and requirements of the petroleum industry—including the occasional necessity to build a refinery on some inhospitable rock, thousands of miles from the resources of industry—has created the specialist contractor to deal with this type of design and construction. The emphasis in such contract work is on detailed planning, well ahead of the proposed construction schedule. The contractors represent a concentration of facilities and expertise from which chemical and other companies can draw. The fluctuations in the construction programme of a specific company are such that it may be inconvenient and uneconomic to maintain a permanent construction organization. The facilities of contractors represent a pool from which individual companies may draw according to their specific needs. The arguments for

calling in a major contractor in any particular instance are clearly a matter for individual judgement, but there is little doubt that the chemical industry has benefited to some extent by an acquaintance with the services that the expert contractor can offer.

One advantage that petroleum chemical manufacture derives from the background philosophy of the oil industry is the traditional freedom with which processes are made available within the industry by licence and royalty agreements. The policy of the traditional chemical industry has been rather more cautious in this respect.

Perhaps the greatest mark of esteem which a process in the classical tradition of chemical synthesis could acquire was the description 'elegant'. Such a description is commonly applied to an indirect synthesis, involving several stages, each of which gives a high yield of product, and commonly including some novel or unexpected feature. The new technology is a little averse to this approach. The tendency now is to seek out the simplest form which a synthesis can be theoretically made to take, and then to try and make it work in practice. All the resources of pressure, temperature and catalytic promotion are brought into play with the aid of the most highly developed materials of construction. Any steps in synthesis which can conceivably be avoided are cut out. All raw materials, other than those represented in the final product, are eliminated as far as possible. In developing this approach it is necessary to accept relatively low conversions, and consequently considerable recycling of reactants. Processes derived in this manner may not, in the classical sense, always be termed 'elegant', but they tend to achieve the maximum degree of economy. The capital costs of these new plants are generally high, but the operating costs are kept down, so that full benefit can be reaped from operating the process on a large scale. Examples illustrating some aspects of this technological approach include the direct hydration processes for the manufacture of ethyl and isopropyl alcohols, the direct oxidation processes to ethylene oxide, the acrolein route to glycerine, and the propylene route to acrylonitrile.

The location of petroleum chemical facilities has until recently been subject to a number of very limiting factors. The U.S.A. had a good start before 1939, because it was alone in possessing raw material resources (in the form of oil fields, natural gas fields and refineries) together with a substantial market for the chemical products. It is not always properly understood that the chemical industry can thrive only in an industrial climate. Only in such a climate will exist the major consumers of its products, which the large-scale operations of petroleum chemical manufacture demand. Moreover the production of chemicals from petroleum involves a considerable consumption of such chemicals as chlorine, sulphuric acid, etc. These are generally available on an economic basis only in an industrial country. The building of refineries in Europe since 1945, and the discovery of substantial natural gas resources, formed the basis for the extension of petroleum chemical production to the European continent. This made quite a slow start, for the chemical industry, based primarily upon coal, was already well entrenched. The expansion in Europe since 1955 has been very rapid, and some indication of this will be found in the final chapter.

The above outline will indicate the difficulties of initiating petroleum chemical manufacture in less industrialized areas, even where the raw materials are cheaply and abundantly available. One is faced with the alternatives of building a plant mainly to meet local needs, in which case it will be so small as to be below the normal economic size (and may require a Government subsidy or some sort of protection to be viable), or of building the plant to an economic size and then to hunt for external markets. Chemical plants are normally more expensive to construct in an underdeveloped country, the techniques of industrial exporting are less highly organized, and most of the nearby markets will probably also be relatively small. Exporting chemicals from an underdeveloped area is therefore a matter of some difficulty. For these reasons, petroleum chemical manufacture has developed fastest and furthest in the areas with a high degree of industrialization, including a well-developed chemical industry.

It is relevant, in this chapter devoted to characteristics of petroleum chemical manufacture, to refer briefly to some of the techniques which are used, and to which reference is made in subsequent chapters. Most of these are borrowed from petroleum technology, and several will be familiar in a more general sense. Amongst the processes of importance in petroleum chemical manufacture are:

(a) *Distillation*

Distillation is a technique of separation which makes use of the difference in volatility or boiling point of different components in a mixture. It is effected in a column containing a series of horizontal

perforated plates or trays spaced inside. The aim is to carry the most volatile component of the mixture away in the vapour phase from the top of the column, and to draw off the least volatile component as a liquid from the bottom (alternatively, according to specific requirements, a side stream may be taken from almost any point up the column). To effect complex or difficult separations, it is probable that more than one column will be required. The term distillation is properly applied only to those operations where vaporization of the liquid mixture yields a vapour phase containing more than one constituent. Where the vapour from a liquid mixture or solution (such as brine, or a glycerine and water mixture containing less than 80 per cent of glycerine) contains only one component, the process is described as evaporation.

Distillation may proceed at atmospheric pressure, under high vacuum, or at elevated pressure, in accordance with the specific requirements of the separation. The industrial significance must be stressed of distillation at very low temperatures. A combination of refrigeration, and operation at moderate pressure, enables the distillation to be effected of components which would be gases in normal circumstances.

In an endeavour to assist the separation effect, it is sometimes necessary to modify the process of simple fractional distillation (sometimes called fractionation), e.g. by adding additional components. This results in such operations as steam distillation, extractive distillation (distillation in the presence of a solvent which becomes the least volatile component of a mixture), and azeotropic distillation (distillation in the presence of a solvent which becomes the most volatile component of a mixture).

(b) *Solvent Extraction*

This is the separation of a component or components of a mixture by the use of a liquid with selective solvent characteristics. This operation is used for the separation of components by types: for example, the separation of aromatics from paraffins.

(c) *Crystallization*

By allowing a component to form crystals from solution, or from a molten mixture, the solid crystals can be separated by filtration or centrifugal separation from the other components.

(d) *Absorption*

This process is a form of solvent extraction. A component of a gas or vaporized mixture is separated by selective absorption, usually in a liquid solvent. The operation is commonly carried out in a packed tower.

(e) *Adsorption*

Certain highly porous materials (e.g. activated charcoal, silica gel) have the power of condensing on their surfaces large amounts of vapours. Where this adsorption can be operated selectively, it represents a technique for the separation of one component from a mixture.

(f) *Cracking*

In petroleum terminology, this means the breaking down of the large hydrocarbon molecules into molecules of lower molecular weight. This is achieved in the absence of air, by high temperature alone (in which case it is called thermal cracking or pyrolysis) or by a combination of high temperature and catalytic activity.

Amongst the low molecular weight products of cracking are the lower paraffins and olefins, which represent major raw materials for chemical production.

Thermal cracking in the presence of substantial quantities of steam is a modification normally designed to provide high yields of unsaturated gases.

(g) *Reforming*

This is a term normally used in petroleum technology to refer to processes designed to upgrade gasoline quality. Straight run gasoline is subjected to thermal or catalytic reforming to modify the molecular structure of its components, so that the final product has a higher anti-knock rating. Reforming is now more commonly carried out catalytically and in the presence of hydrogen.

The term reforming is also used more loosely in connection with a variety of hydrocarbon reactions (e.g. the methane–steam reaction) which will form synthesis gas or town's gas.

(h) *Alkylation*

This term is used to describe a reaction in which a straight-chain or branched-chain hydrocarbon group (called the alkyl group) is united

either with an aromatic molecule, or an unsaturated hydrocarbon group (which may be straight-chain or branched-chain), to form a new complex molecule. In the chemical industry the application of the process is most commonly in the production of alkylated aromatic compounds.

(i) *Isomerization*

This is a process designed to induce a rearrangement of atoms within a particular molecule. In the petroleum field it is commonly applied to the conversion of a normal paraffin to the isoparaffin. Isomerization of methyl cyclopentane to cyclohexane is of significance in the application of catalytic reforming techniques to aromatics production.

(j) *Polymerization*

Polymerization is the process by which molecules can combine together to form larger, and more complex, molecules of the same empirical formula. The single molecule is called the monomer, and the combined molecule the polymer. Where polymerization is restricted to a specific stage, the product may be described as a dimer, for a combination of two monomer molecules. The trimer and tetramer represent respectively combinations of three or four monomer molecules.

The following Table provides definitions of various petroleum fractions to which reference is made in later chapters:

Product	*Boiling Range*	*Hydrocarbon Molecule*
Gas and liquefied gas	up to 25° C	C_1–C_4
Gasoline (petrol)	ca. 20–200° C	C_4–C_{12}
Kerosene	ca. 175–275° C	C_9–C_{16}
Gas oil and Diesel oil	ca. 200–400° C	C_{15}–C_{25}
Lubricating oil	—	C_{20}–C_{70}
Fuel oil	—	C_{10} upwards
Bitumen and coke	—	large molecules

The terminology for the hydrocarbon molecule is expressed in the normal shorthand form. The suffix represents the number of carbon atoms in the relevant molecules. It will be appreciated that these definitions are broad, and that some overlapping in fractions takes place.

Chapter 3

Raw Materials

Introduction

The original basis for petroleum chemical manufacture, as we now understand it, was the availability at refinery locations of olefin-rich gas streams as a result of refinery cracking operations.

Previously to this, natural gas had been used for the production of carbon black, but the more widespread use of natural gas as a chemical raw material, and in particular, its development to the manufacture of other products such as ammonia, followed closely after the earliest units based on refinery gases.

These two sources represent an overwhelming proportion of the raw materials used for petroleum chemicals in the U.S.A. The European pattern has, however, evolved somewhat differently. Both natural gas and refinery gases lack flexibility as raw materials. The production of refinery gases is geared to the requirements of petroleum products in both a qualitative and quantitative sense. The producer of chemicals from such a petroleum source can never, therefore, be sure that the availability of his raw materials will expand as fast as his market for chemicals. In fact his experience in the past few years has been the opposite. The petroleum industry itself is tending to become more and more specialized, and consequently requires an increasing volume of refinery gas for the preparation of special fuels and additives, whereas previously any gases not fed to the chemical plants were likely to be burnt in the refinery boilers. So far as Europe is concerned, therefore (with a larger chemical industry than the U.S.A. in relation to its petroleum and refinery resources), refinery gases represent a somewhat limited supply of raw material in terms of quantities available, more particularly when one is looking to future prospects.

On the European continent, natural gas has been available in very limited quantities until recently. There has been scarcely any significant discovery of natural gas in the United Kingdom to date.

In many areas of Europe, therefore, a third source of petroleum chemical raw material has been developed. This is represented by cracking units divorced from refineries, specifically designed to produce high proportions of olefinic gas streams from liquid hydrocarbon fractions in the range of naphtha to gas oil. These bear some superficial similarities to the older petroleum thermal cracking plants. They are, however, based on a lighter feedstock and are designed to produce the gas fractions in maximum yield rather than the gasoline fractions which were sought by the petroleum plants.

Classification of Raw Materials

From the outline given, it is apparent that the basic raw materials for chemical manufacture are natural gas, refinery gases, and liquid hydrocarbon fractions. To these should be added, to a lesser extent, certain types of wax. The waxes have not yet been mentioned, and form the subject of a separate section at the end of this chapter.

From these basic petroleum raw materials are derived the secondary raw materials, which form the basis of much of the classification used in the second part of this book. Secondary raw materials and their derivation may be summarized as follows:

Acetylene	from cracking or partial oxidation, either of methane in natural gas, or of higher paraffins.
Methane	a major constituent of natural gas.
Higher Paraffins	normally to be defined as ethane, propane and butane, which may be separated from refinery gas streams or natural gas.
Ethylene	present in refinery gas streams. Produced by pyrolysis of propane and ethane (from refinery streams or natural gas) or by thermal cracking of liquid hydrocarbons.
Propylene	from refinery gas streams or by thermal cracking of liquid hydrocarbons.
C_4 Hydrocarbons	from refinery gas streams or by thermal cracking of liquid hydrocarbons.
Higher Olefins	from wax cracking or from shale oil distillates.

The derivation of these secondary raw materials from the basic raw materials is the subject which this chapter treats in outline. Certain aspects of this subject, such as the detailed separation of individual components of C_4 hydrocarbon streams for specialized applications, are dealt with later in association with the derivatives.

The above list of raw materials is by no means comprehensive. Amongst the raw materials of commercial importance may also be included synthesis gas, aromatics, and sulphur compounds. A section of the second part of this book is concerned with the study of such raw materials and their derivatives.

Refinery Gases

Sources of Refinery Gases

Refinery gases may range from hydrogen, at the lower or more volatile end, to hydrocarbons with four carbon atoms in the molecule at the less volatile end. Essentially they include, in addition to hydrogen, the olefins and paraffins within the range indicated, from methane to butane in the case of the paraffins, and from ethylene to the butylenes amongst the olefins. According to circumstances there will be additional components present, usually in small proportions, such as acetylene, certain dienes (notably butadiene), and impurities such as hydrogen sulphide and nitrogen. The hydrogen sulphide is an undesirable impurity in a variety of petroleum processes (and even in fuel gas), and its removal is normally effected at an early stage.

Refinery gases originally used for petroleum chemical manufacture came from the now obsolete process of thermal cracking. Today the three main sources of refinery gases are the processes of crude oil distillation, catalytic cracking and catalytic reforming.

The distillation of crude oil produces a volatile fraction of paraffinic gases. Only a limited proportion of such volatile material is an acceptable component of gasoline, and the major proportion is separated at the distillation stage, a process known as stabilization of the gasoline. Methane, ethane, propane and butane are the main constituents of this gas fraction. The proportion of gas produced will vary very widely between one crude oil and another.

Catalytic cracking has largely taken the place of thermal cracking in the refinery since it will provide a more valuable range of products, and in particular, a higher quality gasoline. A modern 'fluid-bed'

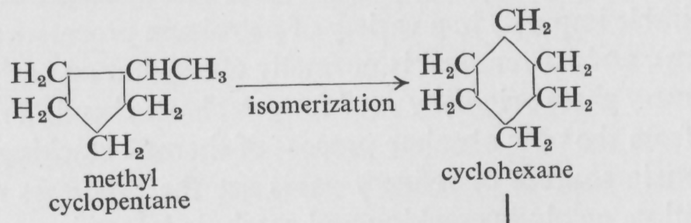
type of catalytic cracker (e.g. one where the control of movement of the catalyst is maintained by the flow of the gases and vapours) uses its catalyst in the form of a fine powder. This catalyst normally consists of alumina and silica in conjunction. Typical yields of gases from this operation are in the Table below. It will be noted that there is a significant proportion of olefins in this gas stream.

Typical Gas Yields from Catalytic Cracking

Feedstock: gas oil
Total gas yield 16·5% wt. of which

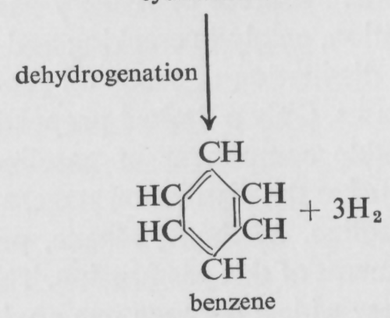
hydrogen is	0·1% wt.
methane is	1·3% wt.
ethylene is	0·6% wt.
ethane is	1·9% wt.
propylene is	2·7% wt.
propane is	2·3% wt.
butylenes are	4·0% wt.
butanes are	3·6% wt.

Catalytic reforming is another process designed to improve the quality of gasoline production. The process is applied to a heavy gasoline fraction including a proportion of naphthenes. In the presence of a catalyst, which is normally platinum-based, the naphthenes will be isomerized and dehydrogenated to produce aromatic compounds. A typical reaction is as follows:



methyl cyclopentane

cyclohexane



benzene

Note: this is commonly abbreviated to

The overall effect is to increase the quality of the gasoline as measured by its anti-knock rating. The reactions take place in a reducing atmosphere, so that, apart from hydrogen, the gas fraction contains only saturated paraffinic compounds (together with a proportion of hydrogen sulphide if sulphur is present in the feed-stock). Typical gas yields obtained from this process are quoted in the Table below. The volatile fraction of this gas stream is rich in hydrogen and can be used with advantage as a raw material for ammonia production.

Typical Gas Yields from Catalytic Reforming

Feedstock: naphtha
Total gas yield 20·0% wt. of which

hydrogen is	0·3% wt.
methane is	1·2% wt.
ethane is	3·5% wt.
propane is	6·3% wt.
butanes are	8·7% wt.

Application of Refinery Gases

In considering the feasibility of producing chemicals from refinery gases one must pay attention to the concept of 'minimum economic size' to which reference has already been made. A small refinery will rarely produce enough of any particular gaseous raw material to justify the building of a chemical plant to use it.

In the case of a substantial refinery, once it is proposed to set up a chemical plant to use one or more components of the gas stream, a complicated gas separation process requires to be installed. Once this gas separation process begins, it tends to become increasingly worthwhile to use other gases which are separated or concentrated at the same time. In this way can be developed an integrated complex of chemical plants, designed to make use of each of the separated gas streams as far as possible.

A substantial section of the whole range of petroleum chemicals is that based on the lower olefins. Even in refineries with a large catalytic cracker there is frequently insufficient of these olefins (particularly ethylene) in the gas streams for a worthwhile chemical development without some form of supplementation.

The production of additional ethylene in a refinery is commonly provided by a separate thermal cracking or pyrolysis operation using

ETHYLENE AND PROPYLENE FROM REFINERY GASES

(Design by The Lummus Company)

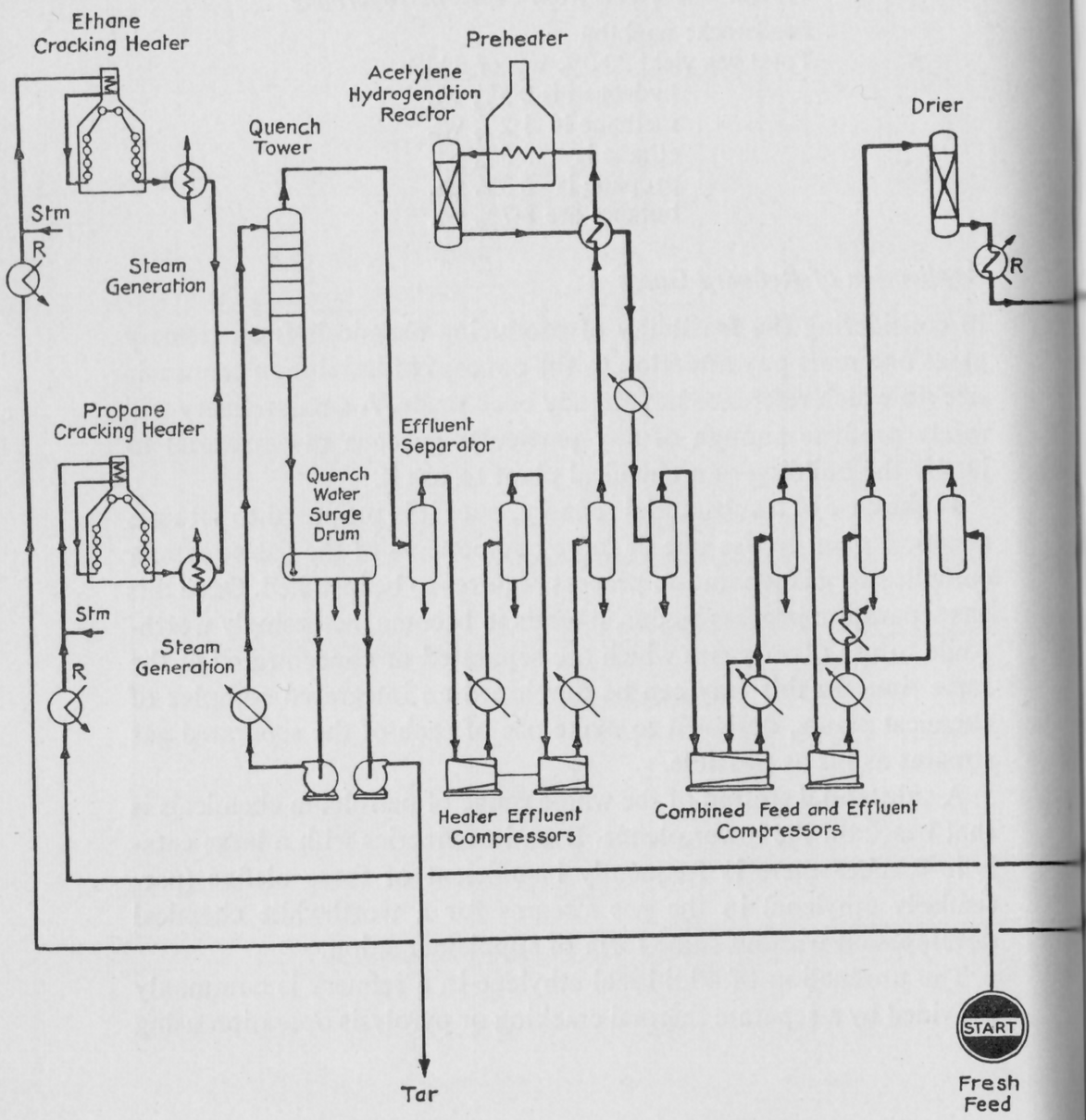
Symbols:

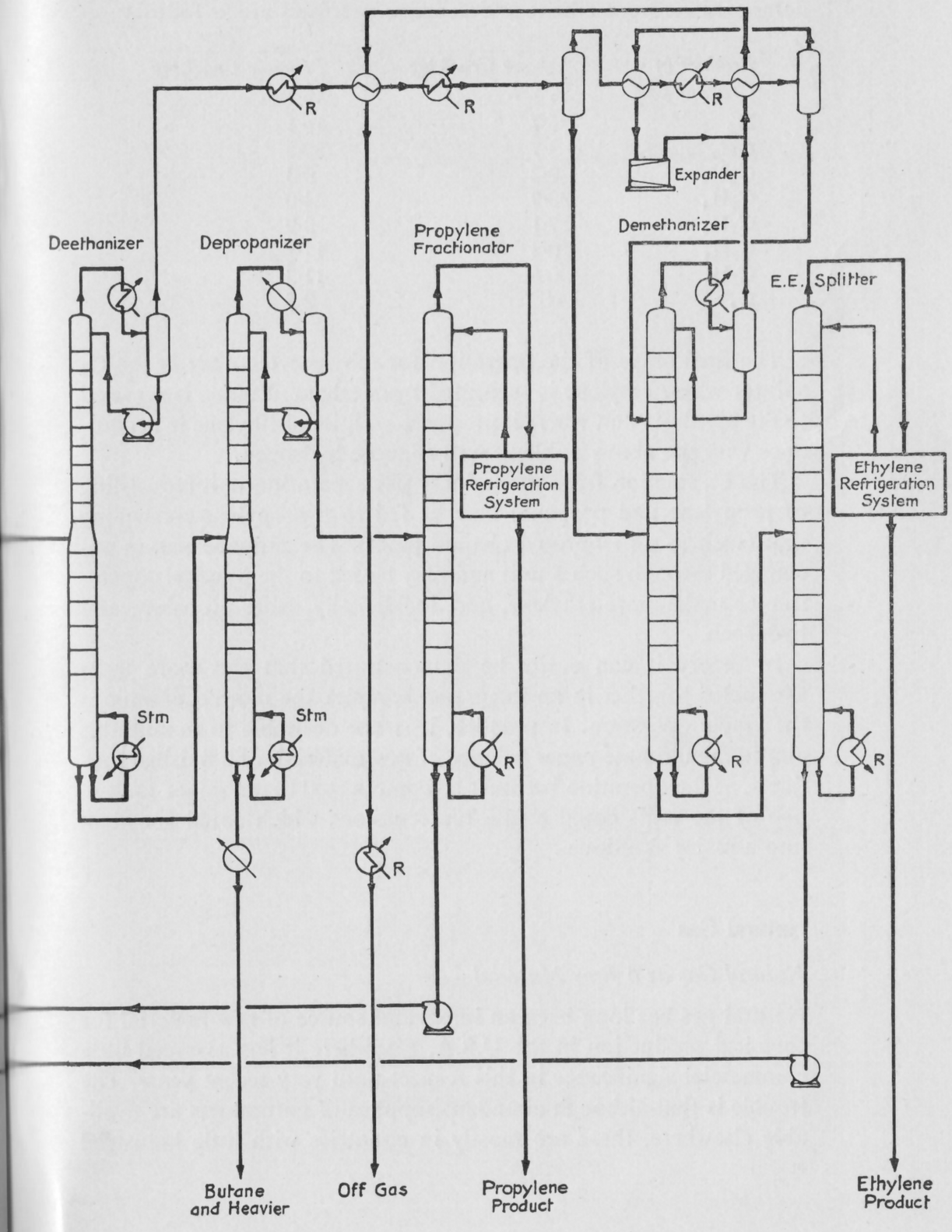
R Refrigerated Chiller

Cooler

R Refrigeration Recuperation

Heat Exchanger





ethane, propane, or both as the charge stock. Typical cracker gas compositions from ethane and propane pyrolysis are as follows:

Product in Cracker Gas	*Ethane Cracking % vol.*	*Propane Cracking % vol.*
H_2	36·7	16·1
CH_4	3·7	30·8
C_2H_2	0·2	0·3
C_2H_4	30·9	24·0
C_2H_6	27·1	3·9
C_3H_6	0·8	11·1
C_3H_8	0·6	11·3
C_4^+	—	2·5

The final stage of the operation for ethylene recovery is the C_2 splitter where ethylene is separated from ethane. Ethane is recycled to the pyrolysis unit where it produces additional ethylene in accordance with the above Table as well as more hydrogen.

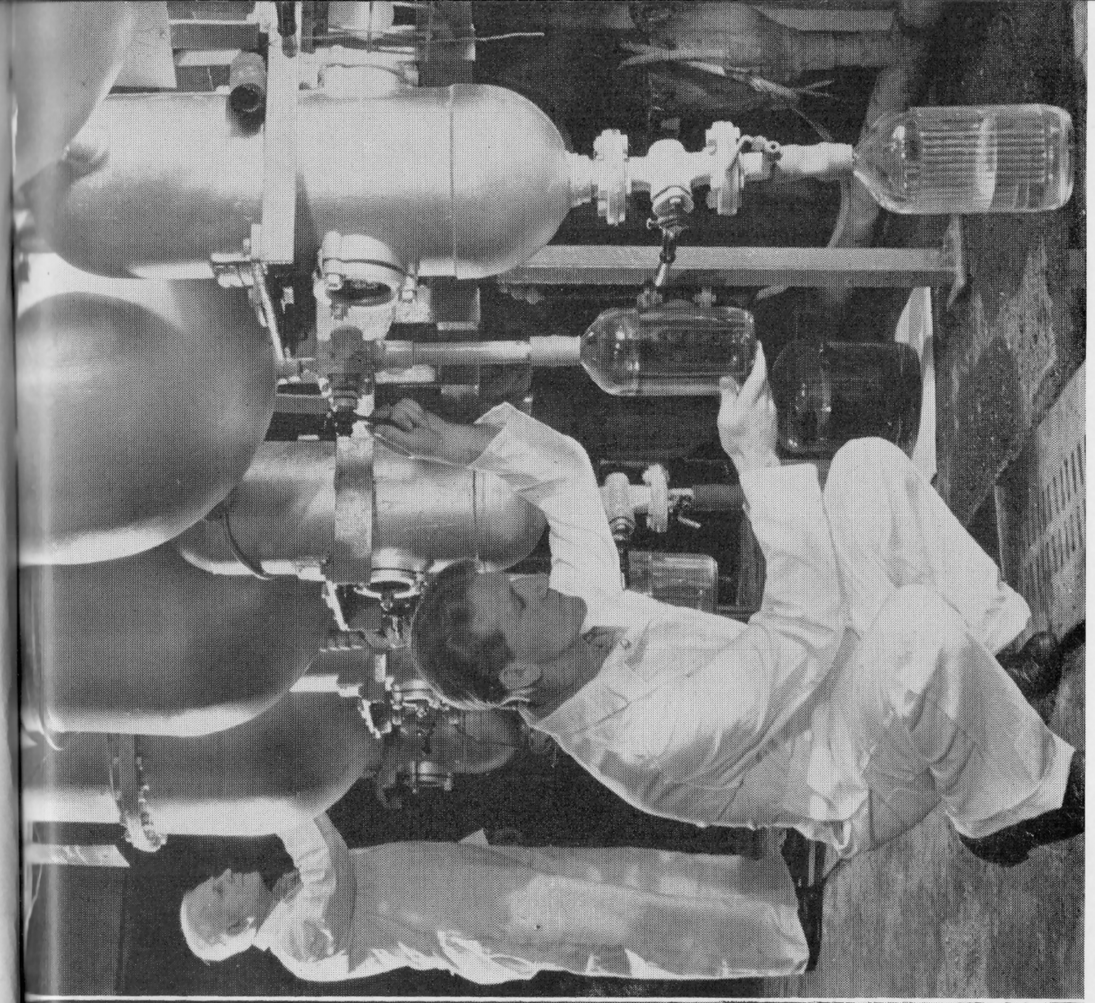
The C_3 fraction from the refinery gas separation unit (consisting of propylene and propane) may be fed to a propylene-consuming unit (such as an isopropyl alcohol plant). The propane passes unchanged through such a unit and may be fed to the pyrolysis operation to make more ethylene, and, incidentally, more propylene and hydrogen.

In theory it can easily be demonstrated that the more units assembled together in an integrated complex the more economic is the whole operation. In practice, it is not desirable to pursue this aim to the ultimate paper balance of raw materials and finished products, as the operation becomes so complicated that a minor fault in one of the units could create repercussions which could snowball into a major shutdown.

Natural Gas

Natural Gas as a Raw Material

Natural gas has long been an important source of raw material for chemical production in the U.S.A. Elsewhere it has assumed little commercial significance in this respect until very recent years. The trouble is that although abundant supplies of natural gas are available elsewhere, these are mostly in countries with little industrial



Fine chemical production
Courtesy A. Boake Roberts & Co. Ltd.
rements of petroleum chemical manufacture are
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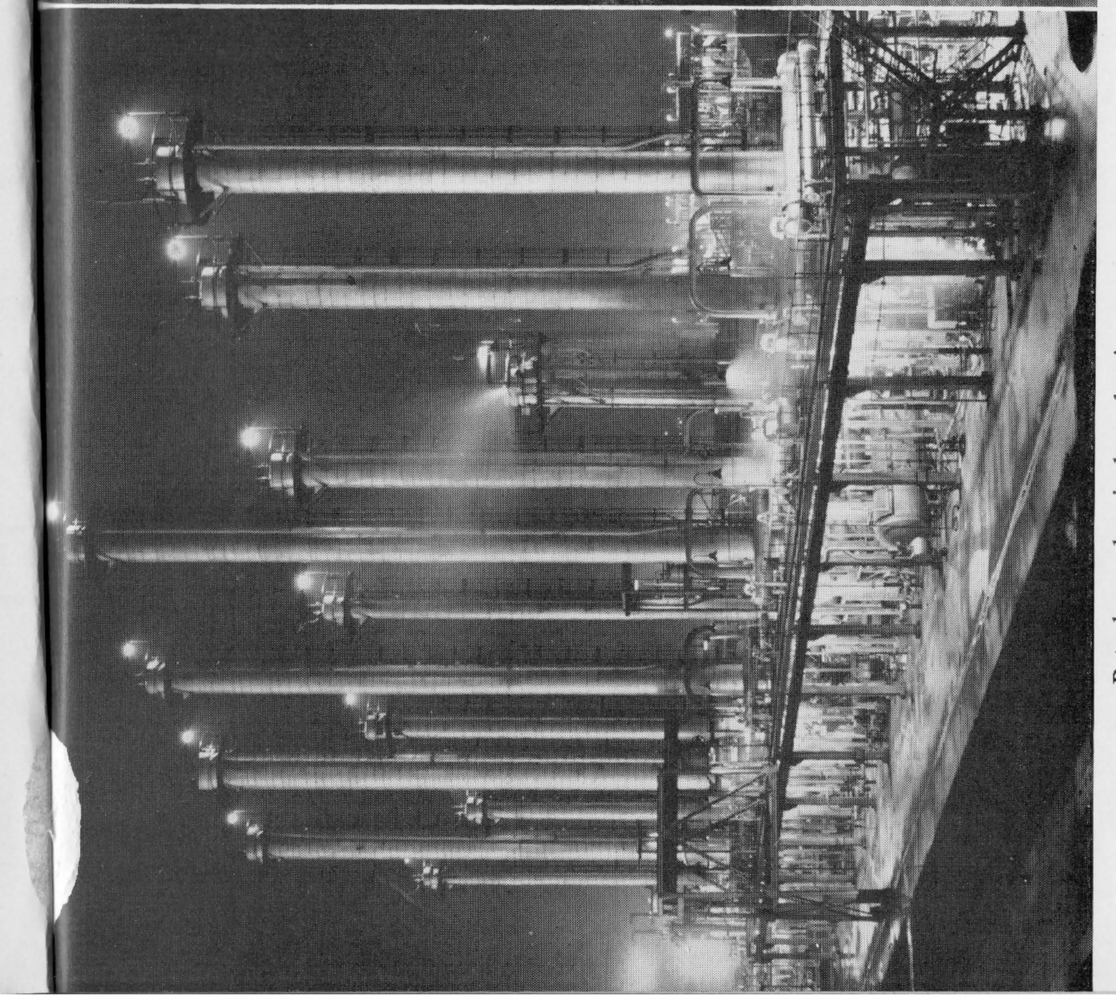
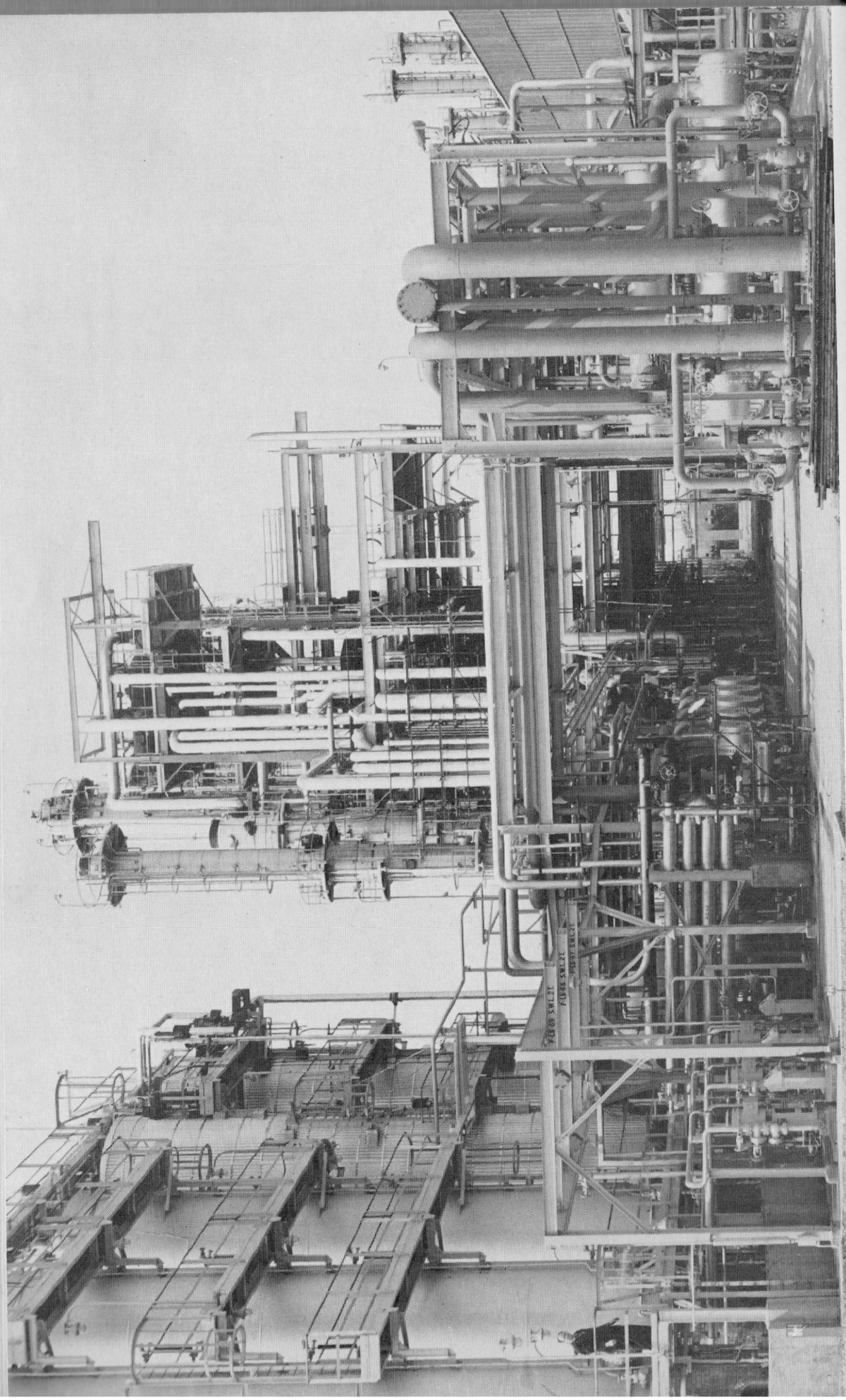


Petroleum chemical production
Courtesy Shell Chemical Co. Ltd.
Both in technique and equipment the requiremen
different from those appropriate to th



Ethylene plant at Grangemouth, Scotland *Courtesy British Hydrocarbon Chemicals*

development, and consequently not offering large scope for the local use of petroleum chemicals. Such countries as Iraq and Venezuela have campaigned for the development of petroleum chemical manufacture based on their natural gas supply, and in the absence of a marked response from commercial interests, have embarked on some preliminary ventures in this field, sponsored by the respective governments.

A development of greater commercial significance at the present time has been the recent discovery of major natural gas fields in Italy and France, and significant new fields elsewhere in Europe, as a result of intensive surveying. Some of the French discoveries are of 'sour' gas containing substantial impurities of sulphur compounds. Until recently, this would have been regarded as a grave disadvantage, but in today's conditions it is enabling France to become one of the world's greatest producers and exporters of sulphur.

Perhaps we should take note here of the current plans for the transport of liquefied natural gas from the Sahara fields to the United Kingdom in special tankers. This material is intended for the production of town's gas, but once the system is established, its application could conceivably be extended to include chemical production.

Natural gas consists essentially of methane, from which can be derived an important but limited range of chemicals. There is usually a significant proportion of higher paraffins. Where these are available in sufficient quantity they can assume considerable importance as potential sources of ethylene by cracking. Apart from hydrogen sulphide present in sour gas, the most common impurities are nitrogen and carbon dioxide in small proportions.

Acetylene from Natural Gas

In considering natural gas as a raw material, it is necessary to take account not only of its major content of methane, but also of its potential for the production of acetylene.

The most common route to acetylene is from calcium carbide, and hence indirectly from coal, according to the reactions:

$$CaO + 3C \rightarrow CaC_2 + CO$$
$$CaC_2 + H_2O \rightarrow CaO + C_2H_2$$

The alternative production of acetylene from hydrocarbons is feasible only where there is a cheap source of the hydrocarbon. The

economics of this operation are usually assisted by the absence of cheap and abundant sources of local coal and power as an alternative. It will be appreciated that whilst calcium carbide can be transported reasonably economically, once the acetylene has been produced, either from carbide or hydrocarbon, economical transport is rarely feasible. The required conditions first arose to a substantial degree in such areas as Germany and the Gulf Coast of the U.S.A. Currently about 28 per cent of the acetylene used for chemicals in the U.S.A. comes from hydrocarbons (largely natural gas). Outside the U.S.A. substantial current developments along similar lines are encountered in Italy and Western Germany, and with the present rapid development of Europe's natural gas resources, more scope may be found in the future for petroleum-based acetylene.

The reaction

$$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$$

begins increasingly to favour acetylene production at temperatures in excess of 1,200° C. There are three basic steps involved in such a process, each offering problems. First, it is necessary to introduce the heat required for the reaction to proceed, secondly the products of the reaction must be cooled very rapidly to prevent decomposition of the acetylene, and thirdly the acetylene must be separated from other reaction products.

In the Huls process the energy input is by means of an electric arc which raises the peak temperature to 1,600° C. The pyrolysed gas is rapidly quenched with water sprays. The separation system employs cyclone separators, water sprays and filters for carbon removal, and water at 19 atmospheres pressure as a selective absorbent for acetylene.

An alternative is the Wulff process employing furnaces in pairs, each containing refractory tiles. Each furnace operates a four-stage cycle in which the tiles are first heated and then used to supply heat for pyrolysis with the operation being repeated in the opposite direction. Having the furnaces in pairs allows the net operation to proceed continuously. The reaction pressure is 0·5 atmospheres and steam dilution is employed to reduce the partial pressure of the hydrocarbon. A peak temperature of about 1,500° C is reached for 0·03 seconds. Quenching with water sprays cools the pyrolysed gas and removes carbon black and tar. The selective solvent used for the recovery of acetylene is dimethylformamide. The Wulff process has

been operated on a substantial pilot plant scale, but is not yet fully commercial.

Perhaps the most important process commercially today is the Sachsse or B.A.S.F.* process, which employs partial oxidation (i.e. controlled oxidation in the presence of a deficiency of the oxidizing medium to prevent the oxidation proceeding to its completion) as the means of providing the energy for the main reaction. The partial oxidation reaction is

$$CH_4 + 1\tfrac{1}{2}O_2 \rightarrow CO + 2H_2O$$

and it is desirable to use oxygen rather than air to avoid unnecessary dilution of the gases to be heated. It is, therefore, necessary to incorporate an air separation unit in the equipment. A specially designed burner provides a reaction temperature of approximately 1,500° C, and the products are immediately quenched to 35° C by water injection. The cracked gases contain 8 per cent volume of acetylene. In the original Sachsse process the selective solvent for acetylene consisted of water under pressure, but more recent versions have switched to methylpyrrolidone. A feature of this process is that the by-product gas contains a substantial proportion of hydrogen and carbon monoxide. These gases, together with nitrogen from the air separation unit, form a suitable basis for ammonia production. The main difficulty lies in the inflexibility in supply of by-product raw materials. It is not always possible to strike an appropriate balance between acetylene and ammonia requirements. Nevertheless, the prospect of project integration of this kind is likely to prove a factor in stimulating further commercial development.

A more recent but important development in this field is the SBA–Kellogg process. This employs the same principle as the Sachsse process, but uses a completely redesigned burner for the partial oxidation and a modified quench assembly. The selective solvent employed in this case is liquid ammonia. A reason why this process is attracting a lot of attention is that it may be adapted to the co-production of acetylene and ethylene which offers useful economic advantages. For production of acetylene and ethylene simultaneously, it is necessary to use higher paraffins than methane (normally a naphtha fraction) as feedstock.

Whilst the reaction of methane has been taken as the basis for

* Badische Anilin und Soda Fabrik.

these operations in the above outline some of the processes are flexible and may use propane or butane as satisfactory alternatives. A further variant is the possibility of using selective adsorption (hypersorption) as a means of aiding acetylene recovery, but solvent extraction is by far the most common technique.

Liquid Hydrocarbons—Cracking Processes

The essence of this exercise is to start with a liquid hydrocarbon, in the naphtha to gas oil range, and to obtain the maximum possible yield of useful olefins including ethylene, propylene, butylenes and probably butadiene, with the minimum formation of coke residues.

Such liquid hydrocarbons have, of course, no precise chemical entity, but it is possible by analysis to calculate an effective formula of the nature CH_x for the mixture. The lighter liquid fractions will exhibit a value for x of about 2·2, whereas for a heavy naphtha this value is approximately 2. As the liquid fraction moves into the gas oil range, the value of x drops below 2 to somewhere in the range 1·8 to 1·9.

There will be a higher proportion of hydrogen in the cracked gases than was originally in the liquid feedstock (together with the production of a liquid fraction with a lower hydrogen content than the feed). The hydrogen content of the liquid feed is likely to be 13–15 per cent weight. Once the hydrogen content of the residual liquids drops to 8 per cent (i.e. a carbon content of 92 per cent) trouble may be anticipated with coking in the furnace or quench devices.

The principle of this operation is very simple. It is similar to the petroleum operation of thermal cracking, except that it is applied to lighter grades of feedstock, and is designed primarily to provide gases rather than gasoline. It therefore uses higher temperatures and lower pressures.

The feedstock is vaporized and rapidly heated, usually with diluent steam, to the cracking temperature, kept at this temperature for a few seconds, and then rapidly quench-cooled to prevent the cracking proceeding too far.

The introduction of steam reduces the partial pressure of the oil vapour in the cracking zone. An important practical effect of this is to increase the proportion of olefins in the gas streams. The precise conditions of temperature, reaction time, and partial pressure require to be adjusted according to the product balance required in the gas fraction. The presence of steam will also tend to minimize the problems of coke formation by virtue of the water–gas reaction (see page 107).

A considerable amount of heat is required so that the feedstock may reach the cracking temperature, and there are three main techniques for providing it. Indirect heating may be provided by passing the vaporized feedstock through tubes inside a gas-fired or oil-fired furnace. Alternatively a cyclic operation is possible (as in Semet–Solvay generators) whereby the heating medium is a checker work which operates on a 'heat and make' cycle. The first part of the run is designed to heat the checker work, and the gas-making run then follows for as long as the necessary temperature can be maintained. Such cycles operated in multiple units enable the process to be effectively continuous.

A third technique is exemplified by the Kellogg adiabatic steam cracking process and in principle uses a heated vapour or gas as the heat carrier. The Kellogg process itself uses steam at over 900° C for this purpose. The naphtha feedstock (vaporized to 680° C) is introduced to the steam, and cracking takes place at oil partial pressures which may be kept down to 1·5 to 2 lb/sq in. Alternatively it is possible to use the steam purely for the partial pressure reduction effect, whilst employing an alternative means of heat input.

We should not leave this subject without some reference to the Catarole process, originally designed to operate catalytically. The emphasis in this operation, unlike all of the others, was on the production of a relatively large liquid fraction with a very high content of aromatic compounds, which could then be separated as pure compounds. As now operated, the Catarole process thermally cracks a highly paraffinic feedstock. A relatively long residence time in the cracker assists in maintaining the high aromatic content of the liquid fraction produced. Current conditions, however, are designed to produce rather more gas and less liquid than the original conception.

Separation Processes

Cracking operations, whether based on refinery propane and ethane, or upon heavier liquid hydrocarbon feedstocks, produce a gas stream

containing a mixture of constituents from hydrogen to the C_4 hydrocarbons.

The technology of gas separation is too complex even to outline here. The basis of the separation is the use of refrigeration and elevated pressures in a combination which can vary very widely. It is then possible to conduct a series of carefully controlled distillation or fractionation operations to separate out the important constituents.

In some cases it may be desirable to augment the distillation function with additional processes, such as selective absorption of one or more components in a liquid adsorbent. Similarly recourse may occasionally be had to the process of hypersorption, which uses a moving bed of activated carbon to adsorb selectively certain components. Sometimes the presence of acetylene may be undesirable, and in such a case it is easier to hydrogenate it than to separate it. Carbon dioxide may also be an undesirable constituent in certain gas streams. This can normally be dealt with by scrubbing with sodium hydroxide in a tower followed by a drying of the gas. Some further specialized techniques for carbon dioxide removal are considered in the section on ammonia production. The necessity for eliminating sulphur compounds from the gas streams has already been mentioned.

Wax Cracking

Wax cracking is a somewhat more specialized operation than the other processes already considered. Wax can be present to an embarrassing extent in some crude oils. This normally necessitates *inter alia* a solvent extraction process from which it is possible to recover the wax in an unrefined form. Some of this crude wax may be refined to be sold commercially as paraffin wax, but a substantial proportion is diverted to the production of chemicals.

The cracking of wax takes place at a temperature rather lower than that of most other cracking operations, of the order of 500° C. The cracking proceeds for a period of time measured in seconds, usually in the presence of steam. A slightly elevated pressure is commonly employed.

The products of cracking, apart from a relatively small proportion of gas and a fraction of fuel oil, comprise olefins in the range C_5–C_{25}.

These are rarely separated into individual compounds, but appropriate fractions are used as a feedstock to the Oxo process, as a raw material for secondary alkyl sulphate detergents, and as an alkyl fraction for certain alkylation processes. These are all discussed in due course.

Part 2

Petroleum Chemical Products and their Applications

A. CLASSIFICATION OF PETROLEUM CHEMICALS ACCORDING TO SOURCE

Chapter 4

Acetylene Derivatives

Of the acetylene manufactured as a raw material for chemical production in the world outside the Communist orbit, it has been estimated that 27 per cent comes from petroleum hydrocarbons (229,000 tons out of 841,000), and the rest from coal. Acetylene from petroleum is concentrated very largely into three areas, U.S.A., Italy and Western Germany. In describing acetylene derivatives as petroleum chemicals we encounter a situation which is repeated many times in this book; the products under discussion may be derived from petroleum or they may not, but the chemistry and technology involved in further processing is normally exactly the same whatever the raw material source. In the United Kingdom all acetylene is based on coal.

The usage of acetylene in the chemical industry is indicated by the following table. The figures are usages of acetylene for chemical production in the U.S.A. in 1956 together with predictions (made in 1957) for 1961 usage.

End Product	*1956*	*1961*
	(millions lb of acetylene)	
Neoprene	158	230
Vinyl chloride	146	260
Per- and trichloroethylene	76	88
Vinyl acetate	44	78
Acrylonitrile	35	122
Miscellaneous	15	65
	474	843

It is clear from the highly unsaturated nature of the acetylene molecule, that there will be little difficulty in persuading it to react. In practice, as with many other reactive compounds, the reactions of acetylene commonly use catalysts not to promote reactivity, but to direct it along one specific route, and to avoid side reactions. The purpose of such catalysts, in short, is selectivity.

Vinyl Chloride

The reaction of acetylene with hydrogen chloride

$$HC{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$$

is carried out in the vapour phase using mercuric chloride on charcoal as a catalyst. The reagents must be pure and dry, with a slight excess of hydrogen chloride. The pressure used is atmospheric, and the temperature may be 100–180° C.

Most of the vinyl chloride produced is polymerized to polyvinyl chloride for the manufacture either of resilient products such as sheeting or flooring materials, or rigid products such as pipes, etc. Pure vinyl chloride can be polymerized in bulk by being subjected to pressure and a temperature carefully controlled at about 60° C. Alternatively vinyl chloride can be polymerized as an emulsion in water to which appropriate catalysts have been added. The polymer produced as an emulsion in water is coagulated and separated. The product is washed and dried.

An associated product is vinylidene chloride. The reaction of chlorine with vinyl chloride produces 1,1,2-trichloroethane, and this, on treatment with sodium hydroxide, becomes vinylidene chloride.

$$\underset{\text{vinyl chloride}}{CH_2{=}CHCl} + Cl_2 \longrightarrow \underset{\text{trichloroethane}}{CH_2Cl{-}CHCl_2} \xrightarrow{+NaOH} \underset{\text{vinylidene chloride}}{CH_2{=}CCl_2} + NaCl + H_2O$$

Vinylidene chloride is used as a copolymer with vinyl chloride to form products with special properties.

An important alternative way of producing vinyl chloride is the process starting from ethylene described on page 72.

For the year 1960 approximately 1,000 million lb of vinyl chloride were produced in the U.S.A., 54 per cent of it from acetylene and the

remainder from ethylene. For the same year the United Kingdom production of polyvinyl chloride approximated to 105,000 long tons.

Vinyl Acetate

Acetic acid vapours are passed with an excess of acetylene at 170–210° C over a catalyst of zinc acetate on charcoal. The pressure is slightly above atmospheric. The exit gases are cooled to 0° C, at which temperature surplus acetylene is separated and recycled. Vinyl acetate is purified by distillation.

$$\underset{\text{acetic acid}}{CH_3COOH} + HC{\equiv}CH \rightarrow \underset{\text{vinyl acetate}}{CH_3COOCH{=}CH_2}$$

Vinyl acetate will polymerize readily either alone or with other vinyl compounds. Polyvinyl acetate finds important applications in the production of adhesives and emulsion paints. Production in the U.S.A. of vinyl acetate reached 285 million lb in 1960. In the United Kingdom, the estimated consumption of vinyl acetate for 1961 is 18,000 long tons.

Neoprene

Neoprene is a synthetic rubber which is notable for its resistance to deterioration in the presence of aliphatic chemicals and hydrocarbons. Neoprene is, in fact, chloroprene or 2-chlorobutadiene.

The first step in the production of Neoprene is the polymerization of acetylene to monovinylacetylene in the presence of acid cuprous chloride.

$$2HC{\equiv}CH \rightarrow \underset{\text{monovinylacetylene}}{HC{\equiv}CHC{=}CH_2}$$

In the presence of aqueous cuprous chloride, monovinylacetylene will add a molecule of hydrogen chloride at 30–60° C to give chloroprene, which is the monomer for Neoprene.

$$\underset{\text{monovinylacetylene}}{HC{\equiv}CHC{=}CH_2} + HCl \rightarrow \underset{\text{chloroprene}}{CH_2{=}CClCH{=}CH_2}$$

This production is carried out on a fairly substantial scale (the 1960 production in the U.S.A. being about 134,000 long tons), but so far has been based almost exclusively on acetylene from coal.

Trichloroethylene

This is another operation which up to the present has mainly used acetylene from coal. The acetylene is first chlorinated in solution in tetrachloroethane. This addition reaction uses a temperature of 80° C and a catalyst of antimony or ferric chloride. The product is 1,1,2,2-tetrachloroethane. This is treated with a slurry of lime at the boil, or by pyrolysis at higher temperatures, with or without a catalyst, to give trichloroethylene.

$$HC{\equiv}CH + 2Cl_2 \longrightarrow \underset{\text{tetrachloroethane}}{CHCl_2{-}CHCl_2} \xrightarrow{-HCl} \underset{\text{trichloroethylene}}{CCl_2{=}CHCl}$$

Trichloroethylene is widely used as a solvent for dry cleaning and metal degreasing. The production in the U.S.A. in 1959 amounted to 360 million lb.

Acrylonitrile

This has been a more recently developed acetylene derivative, and is responsible for consuming a high proportion of the acetylene based on petroleum in the U.S.A. The reaction involved is the addition of acetylene to hydrogen cyanide.

$$HC{\equiv}CH + HCN \longrightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN}$$

The process operates at atmospheric pressure and a temperature of around 70–90° C, in the presence of a catalyst comprising a solution of cuprous chloride in hydrochloric acid. This process is in competition with an alternative route via ethylene oxide. More economical methods of acrylonitrile production are the subject of active research, and an important competitive process based on propylene is expected to develop.

The substantial progress of acrylonitrile in the past few years has made it one of the most important petroleum chemical derivatives. Its uses are associated with fast moving industries. Most acrylonitrile is consumed in the production of acrylic fibres (e.g. Orlon, Acrilan)

which are used for knitwear, suitings, etc. In the plastics industry acrylonitrile may be co-polymerized with other monomers, such as styrene or vinyl chloride, to meet specific requirements in the final product. Acrylonitrile is a raw material for nitrile rubber. This synthetic rubber was of importance in wartime for the construction of self-sealing gasoline tanks for aircraft. Nitrile rubber has the specific property of resistance to aromatic hydrocarbons, and finds more prosaic use today for the hoses of service stations' fuel and gasoline pumps.

The U.S.A. production of acrylonitrile rose from 63 million lb in 1954 to 229 million lb in 1960. In 1960 the usage was as follows:

Acrylic fibres	70%
Nitrile rubber	13·5%
Plastics	12%
Miscellaneous	4·5%

By the end of 1961 the estimated acrylonitrile capacity in the U.S.A. will total 450 million lb/year, of which 63·5 per cent will use acetylene as raw material, 15·5 per cent ethylene oxide, and 21 per cent propylene (not all this capacity is completed at the time of writing). In 1960 acrylonitrile production in the U.S.A. was based 86 per cent upon acetylene and 14 per cent on ethylene.

Usage of acrylonitrile in the United Kingdom has been currently estimated at 12,000 tons per annum. This figure is expected to rise rapidly and reach perhaps 30,000 tons in 1964.

Acetaldehyde and its Derivatives

One of the ways of producing acetaldehyde is by the hydration of acetylene using sulphuric acid in the presence of mercuric sulphate.

$$HC{\equiv}CH + HOH \longrightarrow \underset{\text{vinyl alcohol}}{H_2C{=}CHOH} \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO}$$

The initial product of the reaction is vinyl alcohol, which promptly re-arranges itself to give acetaldehyde. This reaction takes place at roughly atmospheric pressure and 95° C in a rubber-lined tower. Only about 53 per cent of the acetylene fed is reacted and the remainder is recycled, after removal of organic products. This route

to acetaldehyde is gradually being replaced by the ethylene route via ethyl alcohol. The former accounted for only 6·1 per cent of U.S. acetaldehyde production in 1960.

The main consumption of acetaldehyde is in the production of acetic acid and acetic anhydride. The liquid phase oxidation of acetaldehyde to acetic acid is carried out by the use of air or oxygen in the presence of manganous acetate,

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

Reaction conditions using oxygen are 70–80° C and a pressure sufficient to keep the acetaldehyde liquid. Using air, the conditions quoted have been 55–65° C and a pressure of about 5 atmospheres.

A modification of this reaction to allow of the simultaneous production of acetic acid and acetic anhydride is achieved by use of a mixture of copper and cobalt acetates as the catalyst. It is common to add a substantial proportion of ethyl acetate as a diluent. This has the effect of increasing the ratio of acetic anhydride to acetic acid in the product mixture. The reaction conditions may typically be 50–70° C and 5 atmospheres pressure.

$$\underset{\text{acetaldehyde}}{CH_3CHO} + O_2 \rightarrow \underset{\text{peracetic acid}}{CH_3COOOH}$$

$$\underset{\text{peracetic acid}}{CH_3COOOH} + \underset{\text{acetaldehyde}}{CH_3CHO} \rightarrow \underset{\text{acetic acid}}{2CH_3COOH}$$

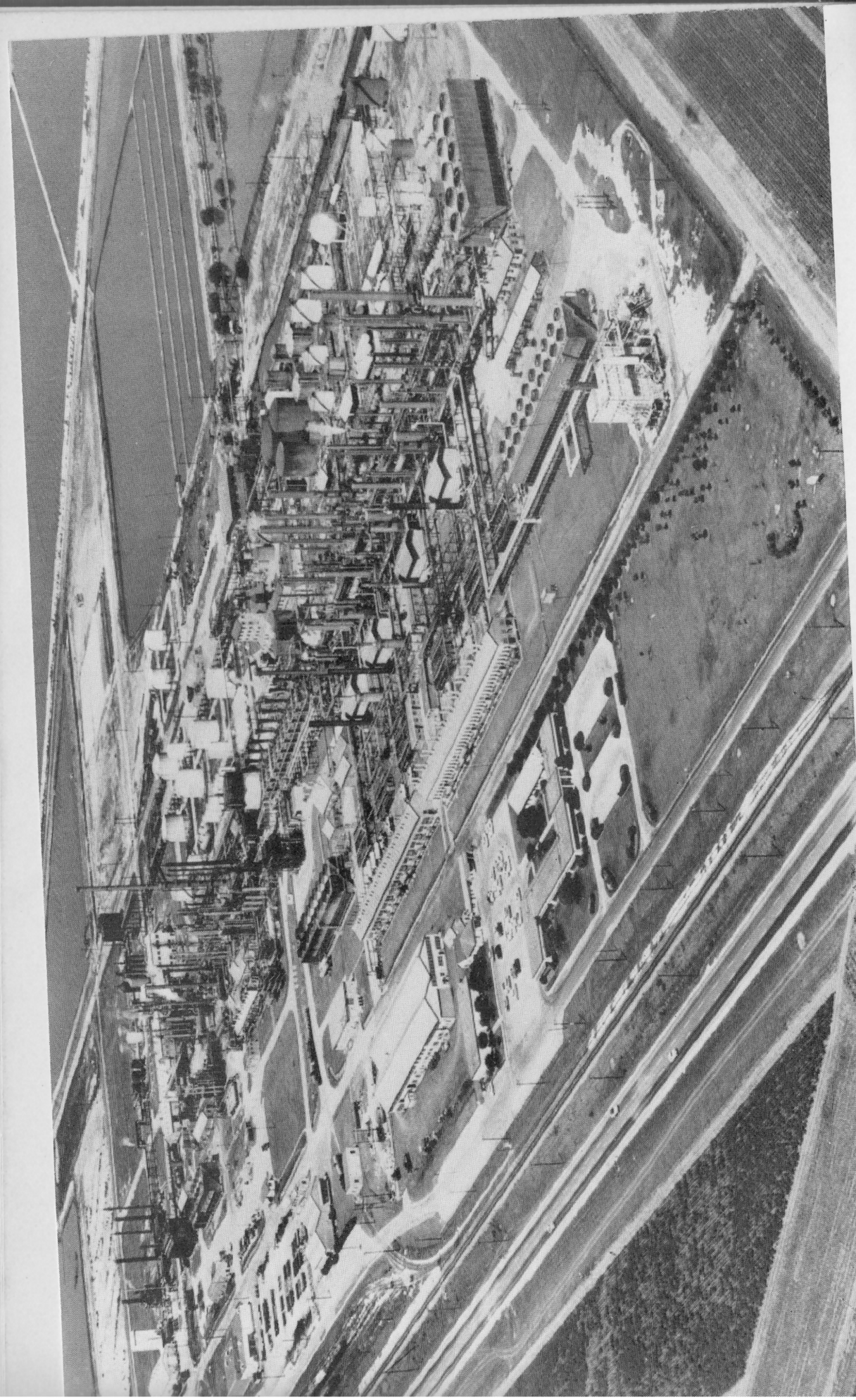
$$CH_3COOOH + CH_3CHO \rightarrow \underset{\text{acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

More than half the acetic acid made is consumed in acetic anhydride production, and another important use is in the production of such esters as ethyl and butyl acetates, which are solvents widely used in the application of industrial lacquers.

There are, in addition to the process described for the joint production of acetic acid and anhydride, two processes for the production of additional acetic anhydride from the acid. The most important one involves catalytic pyrolysis or cracking at a temperature of 700° C and under reduced pressure in the presence of triethyl phosphate as catalyst. The gases from the furnace are condensed, and dilute acetic acid is drawn off at the botton of the condenser. From

Production of acrylonitrile from propylene at Lima, Ohio

Courtesy Standard Oil Co. Ohio



Plant for the oxidation of paraffins at Bishop, Texas *Courtesy Celanese Corporation of America*

the top is drawn off nearly pure ketene. The ketene is immediately reacted with further acetic acid to give acetic anhydride.

$$\underset{\text{acetic acid}}{CH_3COOH} \rightarrow \underset{\text{ketene}}{CH_2{=}C{=}O} + H_2O$$

$$CH_3COOH + CH_2{=}C{=}O \rightarrow (CH_3CO)_2O$$

A second route reacts acetic acid with acetylene. The temperature used is 60–95° C with an acidified mercury catalyst. The immediate product of this reaction is ethylidene diacetate. Sludge is settled from the reaction products, and the clarified liquor is neutralized and treated by vacuum distillation in the presence of an acid catalyst such as sodium pyrophosphate or zinc chloride. Under these conditions ethylidene diacetate is converted to acetic anhydride and acetaldehyde. For this reason the process is particularly convenient to operate in conjunction with a further operation using acetaldehyde as raw material (an obvious possibility is the production of further acetic acid).

$$\underset{\text{acetic acid}}{2CH_3COOH} + \underset{\text{acetylene}}{HC{\equiv}CH} \rightarrow \underset{\text{ethylidene diacetate}}{CH_3CH(OCOCH_3)_2}$$

$$\underset{\text{ethylidene diacetate}}{CH_3CH(OCOCH_3)_2} \rightarrow \underset{\substack{\text{acetic}\\\text{anhydride}}}{(CH_3CO)_2O} + \underset{\text{acetaldehyde}}{CH_3CHO}$$

A very substantial proportion of acetic anhydride is consumed in the production of cellulose acetate. Most of this becomes acetate rayon, but cellulose acetate also has important applications in the plastics field.

The production of acetaldehyde in the U.S.A. amounted to approximately 850 million lb in 1958. The usage was quoted as follows:

	million lb.
Acetic acid	313
Acetic anhydride	40
n-Butanol	230
2-Ethylhexanol	125
Pentaerythritol	22
Butyric acid	20
Miscellaneous	100
	850

In the same year approximately 660 million lb of acetic acid were consumed, as follows:

	million lb.
Acetic anhydride	350
Vinyl acetate	125
Esters	100
Chloroacetic acid	20
Salts	15
Miscellaneous	50

Acetic anhydride was consumed in the U.S.A. in 1958 to the extent of about 360 million lb, on the following basis (net):

	million lb.
Cellulose esters	275
Aspirin	15
Miscellaneous	70

The position of acetaldehyde and its derivatives is considered further in connection with its derivation from ethylene.

Chapter 5

Methane Derivatives

Acetylene See page 24
Ammonia See page 107
Methyl Alcohol See page 117
Carbon Black See page 132

The above derivatives are discussed elsewhere as indicated. Acetylene is treated for convenience as a raw material, and its derivation is, therefore, discussed in the chapter on raw materials. Ammonia, methyl alcohol and carbon black can be derived not only from methane, but from a wide range of alternative hydrocarbons. They are, therefore, excluded from the classification according to source, and examined separately in the subsequent product groups.

Hydrogen Cyanide

This is a long-established product that has developed to an unprecedented extent within the past ten years. Both of the major routes to acrylonitrile currently practised employ hydrogen cyanide. It is also important as a raw material in the production of acrylate plastics, and of the adiponitrile used as an intermediate in the manufacture of nylon.

The petroleum route to hydrogen cyanide is the reaction between hydrocarbons (in practice essentially methane) and ammonia. Sufficient oxygen must be present for the reaction to proceed.

$$2NH_3 + 3O_2 + 2CH_4 \rightleftharpoons 2HCN + 6H_2O$$

Ammonia, air and natural gas (with higher paraffins usually removed) are passed over a platinum catalyst at a pressure slightly above atmospheric and a temperature of about 1,000° C. A consideration of reaction equilibrium would suggest a higher temperature still, but at such high temperatures product decomposition is too rapid. The reacted gases are cooled, and scrubbed with acidified

water to remove ammonia. The hydrogen cyanide is then absorbed in water, and purified and concentrated by distillation.

Previous to the development of the petroleum route, the same basic process had been developed using methane, present in coke oven gas, as a raw material. The major earlier process involved the production of sodium cyanide from sodamide and carbon, and the subsequent acidification of sodium cyanide.

$$\underset{\text{sodamide}}{NaNH_2} + C \xrightarrow{-H_2} \underset{\substack{\text{sodium}\\\text{cyanide}}}{NaCN} \xrightarrow{H_2SO_4} HCN$$

The production of hydrogen cyanide in the U.S.A. has expanded from 4,500 tons in 1947 to 84,500 tons in 1959, and most of this expansion is represented by the petroleum chemical operation, but the earlier processes retain some commercial significance.

There are two alternative processes which have not yet assumed much commercial significance. Given a specifically favourable location, with cheap and abundant supplies of carbon monoxide and methyl alcohol, these processes could become competitive. From the nature of their raw materials it is obvious that these could be largely of petroleum origin.

The indirect process reacts carbon monoxide with methyl alcohol to produce methyl formate (the conditions required are severe; 200 atmospheres, 105° C, and 1 per cent of sodium hydroxide as catalyst). Methyl formate reacts with ammonia at 60–70° C and 10–15 atmospheres pressure, to give formamide together with methyl alcohol. Formamide is dehydrated in the vapour phase at 360° C over aluminium phosphate. The presence of a large excess of ammonia serves to reduce the partial pressure of the formamide thereby favouring the conversion.

$$CO + \underset{\substack{\text{methyl}\\\text{alcohol}}}{CH_3OH} \rightarrow \underset{\substack{\text{methyl}\\\text{formate}}}{HCOOCH_3}$$

$$\underset{\substack{\text{methyl}\\\text{formate}}}{HCOOCH_3} + NH_3 \rightarrow \underset{\text{formamide}}{HCONH_2} + \underset{\substack{\text{methyl}\\\text{alcohol}}}{CH_3OH}$$

$$\underset{\text{formamide}}{HCONH_2} \rightarrow HCN + H_2O$$

A consideration of these reactions will make it clear that the methyl alcohol is essentially redundant, and that a direct reaction is

theoretically feasible. It is therefore characteristic of the modern chemical industry, as we have already pointed out, to attempt to make the simplest possible equation work.

$$CO + NH_3 \leftrightharpoons HCN + H_2O$$

This reaction, in practice, offers a most unfavourable equilibrium, and, moreover, hydrogen cyanide tends to be hydrolysed by the water of reaction. The position may be improved by the use of a large excess of carbon monoxide, so that the overall reaction may become

$$2CO + NH_3 \rightarrow HCN + CO_2 + H_2$$

Such a reaction requires in practice a mol ratio of 20 : 1 of carbon monoxide to ammonia. A temperature of about 700° C is needed, in the presence of a dehydration catalyst such as alumina. This reaction has so far received negligible commercial development, but its basic simplicity is an obvious potential attraction, and further work may be anticipated towards overcoming the practical and economic difficulties.

Methyl Chloride and Methylene Dichloride

These are products of the chlorination of methane. It is possible to extend such an operation to include chloroform and carbon tetrachloride as well. Whilst this is done to some extent commercially, carbon tetrachloride is more commonly made by chlorination of carbon disulphide, and chloroform by reduction of carbon tetrachloride (or from the reaction of bleaching powder on acetone or ethyl alcohol).

Methane is the most difficult of the paraffins to chlorinate. Since methyl chloride itself chlorinates faster than methane, a large excess of methane must be used if a reasonable yield of methyl chloride is to be obtained. In German practice 5 mols of methane (which must be free of ethylene) were reacted with 1 mol of chlorine. The reaction temperature was about 400° C. In this case the condensed reaction mixture contained 50 per cent methyl chloride, 35 per cent methylene dichloride and 15 per cent of more highly chlorinated compounds.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

Where the reaction is to be directed exclusively to methyl chloride, the desirable methane/chlorine mol ratio is 10 : 1, but where all four chlorinated methanes are to be co-produced, the mol ratio may be reduced to 1·7 : 1.

For the production of methyl chloride it is desirable to use a catalyst which is commonly partially reduced cupric chloride on pumice. In other cases the reaction may be promoted by irradiation with ultra-violet light.

Where the proportion of methylene dichloride is to be increased, methyl chloride can be recycled. The limit of recycle is 20 per cent by volume of the total hydrocarbon gas fed, above which excessive carbon formation would result.

Methyl chloride can alternatively be produced by the action of hydrochloric acid on methyl alcohol.

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

Methyl chloride is used as a catalyst solvent in the production of butyl rubber. Its refrigerant applications are becoming less important, but its future seems assured as a chemical reagent in the preparation of silicone resins.

Methylene dichloride has been expanding faster than methyl chloride in recent years. Its main use is as a paint remover, but it is also employed for heat control in the manufacture of cellulose acetate.

The production of methyl chloride in the U.S.A. for 1961 was estimated at 115 million lb, whereas that for methylene dichloride was 125 million lb in 1960.

Chapter 6

Derivatives of Higher Paraffins

The main raw materials considered in this section are ethane, propane and butane. The major applications of ethane and propane for pyrolysis to ethylene have already been discussed. Ethane, propane and butane can be oxidized to synthesis gas (for ammonia or methyl alcohol production) in common with a wide variety of other hydrocarbons.

In this section it is proposed to deal essentially with those products and processes with a specific application to the paraffins quoted. Nitroparaffins are included here for convenience, although the methane derivative is one of the series. Some reactions of paraffins in the C_{10}–C_{18} range are included as a part of the background to the story of synthetic detergent development.

Ethyl Chloride

Most ethyl chloride is made by hydrochlorination of ethylene, but there are two processes in commercial use involving the chlorination of ethane. This is somewhat easier to perform than the chlorination of methane.

In practice, the chlorination of ethane is carried out, using a large excess of ethane, at a temperature of 300–500° C. Since ethyl chloride chlorinates much more slowly than ethane, it is relatively easy to direct the reaction towards the monochlorinated product.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

A practical disadvantage of this process is the formation of by-product hydrogen chloride, which is quite frequently a glut on the market. A modification of this operation has therefore been developed, which combines the reaction above with the hydrochlorination of ethylene. It was found that in the gas phase the chlorination of ethane would proceed in the presence of ethylene without any serious

development of addition reactions. By this means, the chlorine is completely utilized, with a minimum of by-product formation.

$$\underset{\text{ethane}}{C_2H_6} + Cl_2 \rightarrow \underset{\substack{\text{ethyl}\\\text{chloride}}}{C_2H_5Cl} + HCl$$

$$\underset{\text{ethylene}}{C_2H_4} + HCl \rightarrow \underset{\substack{\text{ethyl}\\\text{chloride}}}{C_2H_5Cl}$$

Ethyl chloride finds by far its most important application in the production of tetraethyl lead, which is added to gasoline to improve its anti-knock rating.

Nitroparaffins

These are products of potential, rather than of major commercial importance at this stage.

The commercial development of this range rests largely upon the vapour phase nitration of propane with nitric acid. In the reactor excess propane is treated with sprays of 78–80 per cent nitric acid at 8 atmospheres pressure and 400–450° C. The nitro-products obtained will normally be in the range 10–30 per cent nitromethane, 20–25 per cent nitroethane, 55–60 per cent nitropropanes. The separation is effected in a series of distillation columns. Amongst the lower paraffins the smaller the molecule, the more difficult is the nitration.

It is believed that the reaction proceeds by a free-radical mechanism (the chlorination and oxidation reactions of paraffins are understood to be similar in this respect). The conversion to nitroparaffins may be significantly increased, therefore, by the presence of oxygen or chlorine in the reactor as a source of free radicals.

The nitroparaffins have found some use in the propellant field, and applications are developing as chemical intermediates and solvents, but there is little precise information on the present position.

Oxidation of Propane and Butane

In the normal operation of an industrial chemical process one goes to immense pains to ensure that one or two reactions form the basis of the production, so that subsequent purification is kept as simple as possible. An exception to this rule is the vapour phase oxidation of propane and butane with air as it is carried out in the U.S.A. The

oxidation takes place at temperatures in the range 350–450° C and pressures from 3–20 atmospheres. No catalyst is used.

Something like 15–20 per cent of the hydrocarbon is lost as oxides of carbon. The remaining product mixture includes formaldehyde, methyl alcohol, acetaldehyde, acetic acid, n-propyl alcohol, methyl ethyl ketone, acetone and other oxygenated chemicals.

Reaction conditions and raw materials can be varied to increase the emphasis on one or more selected products from the total range. The problems of separating the pure products are formidable. Here is a case of a process which can scarcely be described as elegant, but which becomes commercially feasible by virtue of basing a simple process on an economical raw material. This is perhaps an extreme case, for the recent trend (outlined below) is towards a greater degree of product control.

A similar operation, rendered more selective by the use of a catalyst (cobalt or manganese acetate), is the liquid phase air oxidation of butane. The conditions are 50–60 atmospheres and 150–250° C. In this case aldehydes are not produced. The major product, according to choice of operating conditions, may be either acetic acid or methyl ethyl ketone.

In 1954, these operations were responsible for 7 per cent of the methyl alcohol and 25 per cent of the formaldehyde made in the U.S.A.

Butadiene from Butane

Butadiene is one of the vital components of the giant synthetic rubber industry (discussed in more detail on page 153). Its production is today one of the largest scale organic chemical operations. The bulk of it is made by dehydrogenation of butylenes. Some butadiene is extracted from gas streams arising from a variety of cracking operations.

The earliest process to be developed on a major scale (apart from the pre-1939 German processes based on acetylene, not now commercially attractive) was that from ethyl alcohol via acetaldehyde.

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$\underset{\substack{\text{ethyl}\\\text{alcohol}}}{CH_3CH_2OH} + \underset{\text{acetaldehyde}}{CH_3CHO} \rightarrow \underset{\text{butadiene}}{CH_2{=}CHCH{=}CH_2} + 2H_2O$$

The final reaction is carried out at 325–350° C, and at atmospheric pressure, over a catalyst consisting of tantalum pentoxide on silica gel. This process has now been largely superseded since it proved uncompetitive with processes based on hydrocarbons, but it has been operated intermittently in recent years.

Butadiene is still produced on an important scale by the dehydrogenation of butane, with the formation of butylenes as a by-product.

$$\underset{\text{butane}}{C_4H_{10}} \rightarrow \underset{\text{butadiene}}{CH_2{=}CHCH{=}CH_2} + 2H_2$$

$$\underset{\text{butane}}{C_4H_{10}} \rightarrow \underset{\text{butylene}}{C_4H_8} + H_2$$

The dehydrogenation takes place at 600–650° C and 0·2 atmospheres in a reactor filled with chromia-alumina catalyst. (This is an illustration of the general principle that for a reaction involving an increase in product volume, the conversion will be increased by operation under reduced pressure, or with the partial pressure reduced by the introduction of a diluent.) The catalyst becomes covered in carbon after perhaps 8–10 minutes. The feed mixture is then directed to another reactor (which has been brought up to cracking temperature) and the carbon is burnt off the catalyst of the first reactor with preheated air. This regenerates the catalyst, after which the reactor is steam purged to eliminate combustion gases. A minimum of three reactors in parallel is therefore required for continuous operation: one on stream, one being regenerated, and one being steam purged. The reactor effluent is oil quenched, stripped of its volatile fraction ('light ends') and the butadiene separated by extractive distillation using furfural, or by extraction (involving formation of a complex) using cuprous ammonium acetate as the extraction medium. Normal fractional distillation cannot be applied to the mixture of C_4 hydrocarbons, since the boiling points are so close together.

Reactions of C_{10}–C_{18} Paraffins

A kerosene cut of boiling range 220–245° C corresponds to n–C_{12}–C_{13} paraffins. It is solvent and acid treated to remove aromatics, and then chlorinated. The chlorination is carried out at 60° C, to give a 50 per cent theoretical conversion to the monochloro-derivative called keryl chloride.

This product may be condensed with an excess of benzene at 50° C using aluminium chloride as catalyst. This operation is known as alkylation, and the product is described as keryl benzene. This was one of the earliest large-scale raw materials for synthetic detergents. The alkyl benzene structure still forms the basis for a large volume of synthetic detergents but the alkyl group now used consists more commonly of propylene tetramer or an olefin fraction and the alkylation catalyst has been changed. The alkyl chain length still approximates to the C_{12}–C_{13} mark.

A similarly obsolete raw material for synthetic detergents is represented by the paraffins of the range C_{10}–C_{18} (originally obtained from German Fischer–Tropsch plants and hydrogenated to remove olefins). The hydrocarbon is reacted with sulphur dioxide and chlorine under exposure to ultra-violet light at normal temperature and pressure. This is known as the Reed reaction

$$RH + SO_2Cl_2 \rightarrow RSO_2Cl + HCl$$ (where R is a hydrocarbon radical)

and is believed to proceed through a free-radical mechanism. The monosulphonyl chloride is called Mersol, and this is reacted with sodium hydroxide to give the sodium sulphonate or Mersolate. Products based on Mersolate were very important in Germany during the second world war, when there was acute shortage of oils and fats for soap making.

Chapter 7

Ethylene Derivatives

Ethylene has proved to be one of the most versatile petroleum chemical raw materials. In scale of operation and variety of products it is the most important of the lower olefins. The tables below give an indication of the usage of ethylene both in tonnage and in terms of major derivatives.

ETHYLENE CONSUMPTION FOR CHEMICALS (IN MILLIONS OF LB) IN U.S.A.

1955	*1958*	*1959*	*1961 (est.)*	*1965 (est.)*
3,000	4,200	4,900	6,000	7,500

CONSUMPTION OF ETHYLENE ACCORDING TO END USE (AS %) IN U.S.A.

	1950	*1958*	*1961 (est.)*	*1965 (est.)*
Ethylene oxide	30	29	26	26
Ethyl alcohol	32	22	19	18
Polyethylene	4	17	26	25
Halogen derivatives	11*	13	12	14
Ethyl benzene (styrene)	12	10	9	11
Miscellaneous	11	9	8	6

* ethyl chloride only

CONSUMPTION OF ETHYLENE ACCORDING TO END USE IN OTHER COUNTRIES IN 1960

	UNITED KINGDOM		*FRANCE*		*WEST GERMANY*	
Product	*Tons ethylene*	%	*Tons ethylene*	%	*Tons ethylene*	%
Ethyl alcohol	47,000	21·4	—	—	—	—
Ethylene oxide	52,000	23·6	15,000	30·6	55,000	33·3
Polyethylene	101,000	46·0	18,000	36·9	60,600	36·7
Styrene	12,000	5·5	9,500	19·4	29,400	17·8
Others	8,000	3·5	6,400	13·1	20,000	12·2
	220,000		48,900		165,000	

In 1959 Canada consumed a total of 80,000 tons of ethylene, and the capacity for ethylene production reached 156,000 tons per annum in 1960.

The ramifications of ethylene chemistry are such as to make it necessary to deal with the derivatives under separate headings, which will themselves require subdivision in certain cases.

Ethyl Alcohol

Production of Ethyl Alcohol

In many countries, the great bulk of ethyl alcohol is still obtained by fermentation processes. Where there is an unquestioned surplus of fermentable material (molasses, grain, starch, wine residues, etc.) of negligible value the fermentation process remains competitive. Once the element of doubt creeps in, the value of the supposedly surplus products becomes unpredictable. An example of this has been molasses from some sugar-producing areas, which has in the past represented an important raw material for ethyl alcohol. Once conditions of low and stable prices for raw material are in doubt, the whole economic basis of the fermentation process for ethyl alcohol comes into question. Today approximately 90 per cent of U.S.A. ethyl alcohol and 75 per cent of the U.K. product is made synthetically. The production in 1960 was about 800,000 long tons in U.S.A., and 100,000 in the United Kingdom.

There are two main processes for the synthesis of ethyl alcohol from ethylene. The earliest to be developed is a process of the concentration–dilution type. This involves the initial absorption of ethylene into 90–98 per cent sulphuric acid at a temperature of 85° C and a pressure of 12–30 atmospheres according to the ethylene content of the gas stream. The ethylene gas stream, which should be free from higher olefins, may contain 40–95 per cent by volume of ethylene. The liquor resulting from the ethylene absorption is a mixture of monoethyl and diethyl sulphates. The mixed esters are pumped to a hydrolyser, together with an appropriate volume of water. Hydrolysis takes place using steam heating. The mixture then contains ethyl alcohol, dilute sulphuric acid, and small amounts of ethyl ether (5–10 per cent of total production) and other by-products, and this passes to a stripping column, where steam carries the volatile

components overhead, allowing dilute sulphuric acid to be drawn off at the bottom.

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow \underset{\text{monoethyl sulphate}}{C_2H_5OSO_2OH}$$

$$2CH_2{=}CH_2 + H_2SO_4 \rightarrow \underset{\text{diethyl sulphate}}{C_2H_5OSO_2OC_2H_5}$$

$$C_2H_5OSO_2OH + C_2H_5OSO_2OC_2H_5 + 3H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

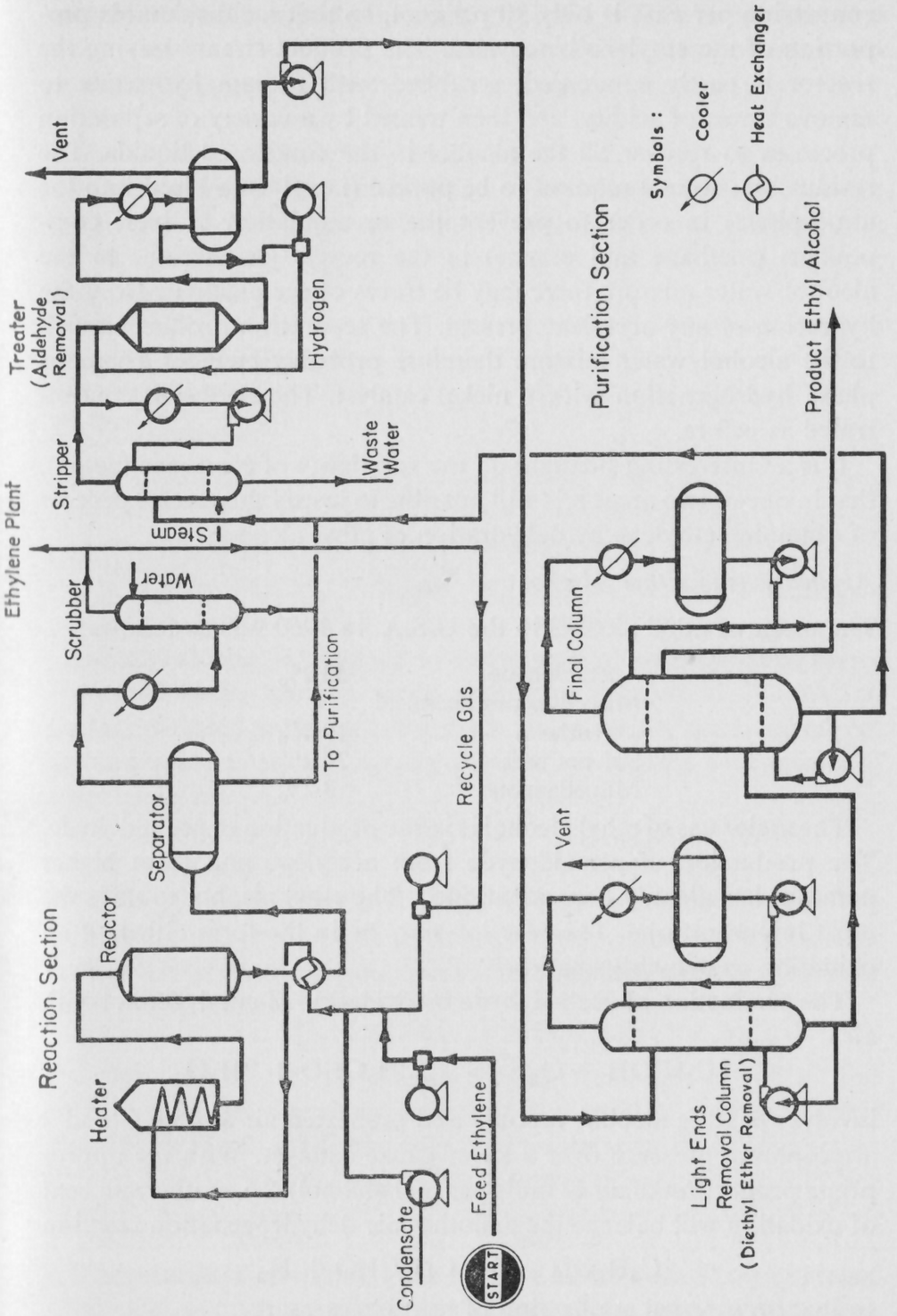
The acid is concentrated by vacuum evaporation and re-used. The crude alcohol vapour from the top of the stripping column passes to a scrubber to remove traces of acidity. Ethyl ether is removed by steam in a distillation column, and the alcohol passes to a fractionating column, from which an azeotrope with water containing 95·6 per cent volume alcohol is taken overhead.

Where anhydrous alcohol is required, the 95·6 per cent azeotrope may be distilled with benzene. The benzene forms a ternary azeotrope with alcohol and water boiling at 69·7° C and also a binary azeotrope with alcohol boiling at 72·5° C. These are separated from the anhydrous alcohol boiling at 78·4° C.

A more recent synthesis process is designed to eliminate the use of sulphuric acid. This is the direct hydration process; it typifies the modern trend towards the most direct possible synthesis route.

$$CH_2{=}CH_2 + H_2O \leftrightharpoons C_2H_5OH$$

In this case the olefin stream will contain about 97 per cent of ethylene (the impurities including methane, ethane, acetylene and higher olefins). It is perhaps necessary to stress that in a recycle process of this kind it is always desirable to minimize impurities (even if they are merely diluents) in the feed. Such impurities will accumulate in the recycle streams and they require a systematic purge (or exhaustion to atmosphere) to prevent such a build-up taking place. The purge always occasions some loss of valuable raw material. The ethylene is compressed to 68 atmospheres, and mixed with a stream of water. The mixture is reacted in the vapour phase at 300° C over a catalyst of phosphoric acid on silica. The choice of conditions is dictated by the familiar conflict of economic requirements. As the temperature increases, the rate of reaction increases, but the equilibrium concentration of ethyl alcohol decreases. The ethylene



ETHYL ALCOHOL FROM ETHYLENE BY DIRECT HYDRATION
(Design by Shell Development Company)

conversion per pass is only 30 per cent, so that a considerable proportion of the ethylene is recycled. The product stream leaving the reactor is partly condensed, scrubbed with sodium hydroxide to remove traces of acidity, and then treated by a variety of separation processes to recover all the alcohol in the condensed liquids. The residual gas stream requires to be purged (i.e. given a bleed into the atmosphere) in order to prevent the accumulation of inert components (methane and ethane) in the recycle gas stream. In the alcohol/water mixture there may be traces of acetaldehyde from the hydration of any acetylene present. The separation process applied to the alcohol/water mixture therefore probably includes a vapour phase hydrogenation with a nickel catalyst. The alcohol is concentrated as before.

It is an interesting sidelight on the variability of economic factors, that in one or two areas it is still possible to justify the reverse process of obtaining ethylene by dehydration of ethyl alcohol.

Applications of Ethyl Alcohol

The usage of ethyl alcohol in the U.S.A. in 1960 was as follows:

Acetaldehyde	53·2%
Miscellaneous chemical synthesis	19·4%
Solvent uses	24·2%
Miscellaneous	3·2%

The major use of ethyl alcohol is in the production of acetaldehyde. The production of acetaldehyde from acetylene and from higher paraffins has already been mentioned. The ethyl alcohol route is the most important one. The reaction may be in the form either of an oxidation or dehydrogenation.

The production of acetaldehyde by oxidation of ethyl alcohol with air

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O$$

involves passing alcohol vapours and preheated air at 450° C and 3 atmospheres pressure over a silver gauze catalyst. With the appropriate proportion of air (2 mols per mol alcohol) the exothermic heat of oxidation will balance the endothermic dehydrogenation reaction

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

so that no external application of heat is necessary.

The dehydrogenation process, which is more common, requires a

chromium-oxide-activated copper catalyst. The temperature is maintained at 270–300° C. The fairly pure hydrogen stream can have useful applications.

With either process the acetaldehyde is separated by distillation from the unreacted alcohol, which is recycled.

The main outlet for acetaldehyde, as has already been pointed out (page 39), is for the production of acetic acid and anhydride. A further important application is in the production of butanol or butyl alcohol.

Acetaldehyde may be dimerized at 20° C in the presence of dilute alkali to form acetaldol.

$$\underset{\text{acetaldehyde}}{CH_3CHO} + CH_3CHO \rightarrow \underset{\text{acetaldol}}{CH_3CH(OH)CH_2CHO}$$

The aldolization is allowed to proceed to 60 per cent conversion. The catalyst is neutralized, a slight excess of acid added, and acetaldol dehydrated in a two-column distillation unit.

$$\underset{\text{acetaldol}}{CH_3CH(OH)CH_2CHO} \rightarrow \underset{\text{crotonaldehyde}}{CH_3CH{=}CHCHO} + H_2O$$

n-Butyl alcohol is obtained by the vapour phase hydrogenation of crotonaldehyde, using a nickel-chromium catalyst at 180° C and slightly elevated pressure. n-Butyl alcohol is mainly used, directly or as the acetate ester, as a lacquer solvent, but it has a wide spread of industrial uses.

$$\underset{\text{crotonaldehyde}}{CH_3CH{=}CHCHO} + 2H_2 \rightarrow \underset{\text{n-butyl alcohol}}{CH_3CH_2CH_2CH_2OH}$$

Turning from the production and derivatives of acetaldehyde, the second most important application of ethyl alcohol is as a solvent in such preparations as lacquers, varnishes, cellulose nitrate, cosmetics, toilet preparations and so on.

Ethyl alcohol is converted to ethyl chloride by heating it with hydrogen chloride in the presence of zinc chloride at 145° C and slightly elevated pressure. This was the original route to ethyl chloride. It is still used, but only on a minor scale.

$$\underset{\substack{\text{ethyl}\\\text{alcohol}}}{C_2H_5OH} + HCl \rightarrow \underset{\substack{\text{ethyl}\\\text{chloride}}}{C_2H_5Cl} + H_2O$$

The esterification of ethyl alcohol and acetic acid, in the presence of a catalyst such as sulphuric acid, produces ethyl acetate. The equilibrium conversion is about 67 per cent. The reaction may be

forced to completion by removing the water formed and employing one reactant in excess.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} \leftrightharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Whilst the esterification route to ethyl acetate is the most common, it is possible to employ the Tischtschenko synthesis of esters from aldehydes (a variant of the Cannizzaro reaction). Acetaldehyde in the presence of some ethyl acetate and ethyl alcohol will condense to ethyl acetate using aluminium ethoxide as catalyst at a temperature of 0° C.

$$\underset{\text{acetaldehyde}}{2CH_3CHO} \rightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5}$$

Ethyl acetate is an important solvent with a wide use in the lacquer industry. In more recent years it has encountered strong competition from methyl ethyl ketone.

Historically, ethyl alcohol was of importance as one of the first major raw materials used to make butadiene for synthetic rubber as described on page 47.

Ethylene Oxide

Production of Ethylene Oxide

There are two methods for the production of ethylene oxide in large-scale operation. The earliest to become established uses ethylene chlorohydrin as an intermediate product.

The chlorohydrin reaction takes place in a tower with or without packing. Ethylene, chlorine and water are introduced to the tower, in which a temperature of about 50° C is maintained. Temperature control is effected by the flow of raw materials and no external heating is required. The actual reaction is between hypochlorous acid and ethylene. Chlorine with water undergoes the reaction

$$Cl_2 + H_2O \leftrightharpoons HOCl + HCl$$

In practice the actual proportions of acid in the mixture are low. The addition of hypochlorous acid to ethylene proceeds more rapidly than the alternative direct addition of chlorine to ethylene, which is unwanted in this case. Provided a slight excess of ethylene is maintained, a concentration of up to 6 per cent of chlorohydrin can be reached before any appreciable amount of ethylene dichloride is derived from the chlorine addition. The chlorohydrin reaction is:

$$CH_2{=}CH_2 + Cl_2 + H_2O \rightarrow \underset{\text{ethylene chlorohydrin}}{\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix}} + HCl$$

The liquid stream (which is corrosive in character) is drawn off at the top of the tower, and treated with a 10 per cent solution of milk of lime in slight excess. The mixture is heated and agitated with live steam.

$$\underset{\text{ethylene chlorohydrin}}{\begin{matrix}2CH_2OH\\|\\CH_2Cl\end{matrix}} + Ca(OH)_2 \rightarrow \underset{\text{ethylene oxide}}{2CH_2{-}CH_2\ (\text{O bridge})} + CaCl_2 + 2H_2O$$

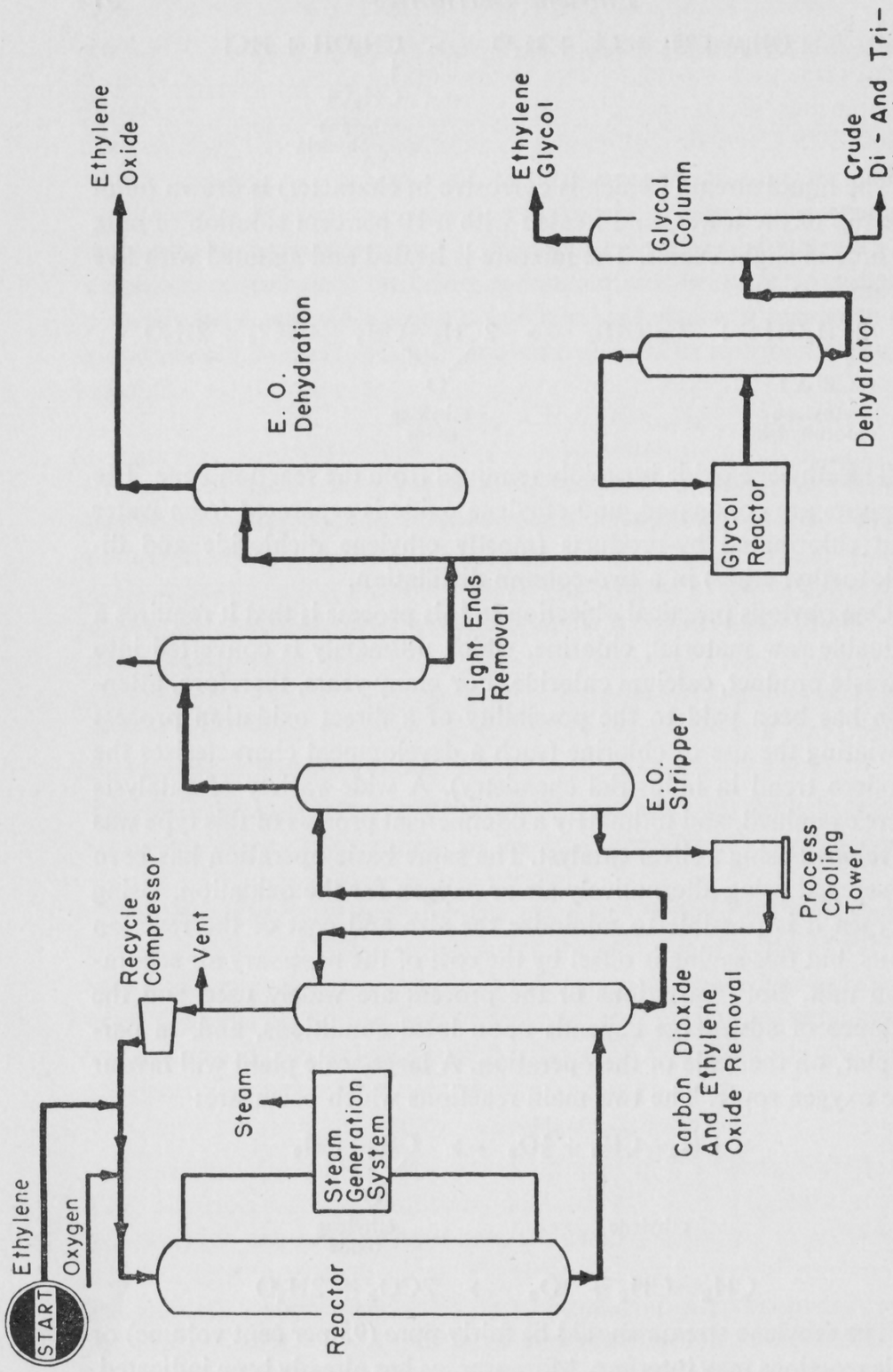
The ethylene oxide is rapidly removed from the reaction zone. The vapours are condensed, and ethylene oxide is separated from water and chlorinated by-products (mostly ethylene dichloride and dichloroethyl ether) in a two-column distillation.

One obvious practical objection to this process is that it requires a valuable raw material, chlorine, which ultimately is converted into a waste product, calcium chloride. For many years, therefore, attention has been paid to the possibility of a direct oxidation process obviating the use of chlorine (such a development characterizes the modern trend in industrial chemistry). A wide variety of catalysts were examined, and ultimately a commercial process of this type was developed using a silver catalyst. The same basic operation has been developed using alternatively air or oxygen for the oxidation. Using oxygen it is possible to minimize the size and cost of the reaction units, but this saving is offset by the cost of the necessary air separation unit. Both variations of the process are widely used and the balance of advantage depends upon local conditions, and, in particular, on the scale of the operation. A large-scale plant will favour the oxygen route. The two main reactions which occur are:

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + \tfrac{1}{2}O_2 \rightarrow \underset{\text{ethylene oxide}}{CH_2{-}CH_2\ (\text{O bridge})}$$

$$CH_2{=}CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

The ethylene stream should be fairly pure (95 per cent volume) or side reactions may interfere. Moreover, as has already been indicated,



ETHYLENE OXIDE BY DIRECT OXIDATION PROCESS, AND HYDRATION TO ETHYLENE GLYCOL
(Design by Shell Development Company, only major equipment illustrated.)

any recycle process needs reasonably pure reactants if it is to avoid elaborate and wasteful purge treatments to prevent the build-up of impurities in the recycle streams. The temperature is commonly 260–290° C for air oxidation, or nearer 230° C where oxygen is used. The pressure may range from atmospheric up to about 10 atmospheres.

The ethylene oxide is isolated by scrubbing the reaction gases with water at atmospheric or higher pressure. The ethylene oxide is subsequently stripped from solution and purified by distillation.

Strict control of the reaction conditions is necessary to minimize loss of ethylene as carbon dioxide in accordance with the second of the equations above.

In comparing the two processes, there is an obvious advantage to direct oxidation in the elimination of the use for every 1 lb of ethylene oxide in the chlorohydrin process of 2 lb of chlorine and 2 lb of lime. On the other hand, the chlorohydrin route requires only 0·9 lb of ethylene per lb of ethylene oxide, against 1·0 to 1·1 lb of ethylene in direct oxidation. Also, direct oxidation plants are, size for size, somewhat more expensive to build. Nevertheless, the general trend is clear enough. Nearly all the ethylene oxide plants built in the past five years are employing the direct oxidation process.

In 1960 ethylene oxide production was approximately 670,000 long tons in the U.S.A. and 55,000 long tons in the United Kingdom.

Applications of Ethylene Oxide

The relative importance of various applications of ethylene oxide is indicated in the following tables.

USAGE IN U.S.A. IN 1960 (estimated)

Ethylene glycol	60%
Non-ionic surface active agents	11%
Ethanolamines	10%
Polyethylene glycols	9%
Acrylics	7%
Glycol ethers	3%

USAGE IN FRANCE IN 1960 (estimated)

Ethylene glycol	46%
Ethanolamines	20%
Polyethylene glycols	8%
Others	26%

The proportion of the total ethylene oxide usage attributable to ethylene glycol varies significantly from country to country. The ethylene glycol market depends to a substantial extent on its use as an anti-freeze in car radiators. This usage will clearly vary according to the concentration of cars in a given country, and also according to the severity of the winter conditions. Most of the major industrialized countries are now becoming highly motorized, but differences of climate will always remain to affect this particular market. Additional factors which are likely to assume increased importance in the future include the arrival of sealed automotive cooling units in the U.S.A. and the popularity of air cooling in certain European countries. Alternative markets for ethylene glycol include the production of polyester fibres and film (e.g. Terylene, Dacron, etc.), for use in the manufacture of industrial explosives, and in regenerated cellulose film (or Cellophane) production.

Some ethylene glycol is obtained as a by-product in the direct oxidation process for ethylene oxide. Most ethylene glycol is made from ethylene oxide by hydration.

$$\underset{\text{ethylene oxide}}{CH_2{-}CH_2 \diagdown\!\diagup O} + H_2O \rightarrow \underset{\text{ethylene glycol}}{HOCH_2CH_2OH}$$

The hydration of ethylene oxide is carried out in the liquid phase (sometimes with an acid catalyst) at atmospheric pressure and 50–100° C, or at about 200° C under pressure, but without a catalyst. An excess of water is employed to minimize the inevitable formation of polyglycols (principally diethylene glycol and triethylene glycol). The crude reactor product is concentrated to 70 per cent glycols by evaporation. The subsequent distillation procedure is complex, since water has to be eliminated, and the individual glycols separated in a pure and marketable condition.

A significant proportion of ethylene glycol is made by a wholly different process from formaldehyde and carbon monoxide. The reactions, briefly, are:

$$\underset{\text{formaldehyde}}{CH_2O} + CO + H_2O \rightarrow \underset{\text{glycollic acid}}{CH_2OHCOOH}$$

$$CH_2OHCOOH + \underset{\text{methyl alcohol}}{CH_3OH} \rightarrow \underset{\text{methyl glycollate}}{CH_2OHCOOCH_3} + H_2O$$

$$CH_2OHCOOCH_3 + 2H_2 \rightarrow \underset{\text{ethylene glycol}}{CH_2OHCH_2OH} + CH_3OH$$

Carbon monoxide, formaldehyde and water react to glycollic acid at 200° C and 700 atmospheres pressure, using sulphuric acid as a catalyst. The glycollic acid is esterified with methyl alcohol, and the ester reacted with hydrogen in the vapour phase, with a chromite catalyst present. The hydrogenation conditions are 200° C and 30 atmospheres pressure. This process accounts for something like 15 per cent of the ethylene glycol produced in the U.S.A. Once again it may be claimed for inclusion in the petroleum chemical field, since the basic raw materials are methyl alcohol (from which most formaldehyde is made) and carbon monoxide.

The co-products of ethylene oxide hydration, diethylene glycol and triethylene glycol, are both industrial products of significance in their own right. Diethylene glycol is used as a humectant, as a selective solvent (notably in the Udex process for concentration of aromatics), and in hydraulic brake fluids. Its esters are used for plasticizers and polyester resins. Triethylene glycol is a component of hydraulic brake fluids, and is used in the chemical sterilization of air.

Polyethylene glycols are made by continuing the reaction between ethylene oxide and ethylene glycol or diethylene glycol. The reaction takes place at 120–150° C and 3 atmospheres pressure, with the assistance of an alkaline catalyst such as sodium hydroxide. According to molecular weight, the polyethylene glycols are liquids or waxy solids. The lower molecular weight products are brake fluid components, and find important applications as plasticizers and humectants in the production of transparent adhesive tapes. The medium and higher molecular weight products are lubricants in the processing of textile fibres, and components of pharmaceutical and cosmetic formulations.

Ethylene oxide will react with alcohols, in the presence of excess alcohol and a catalyst, which may be sodium hydroxide or boron trifluoride according to the alcohol being treated. The conditions vary according to the alcohol being reacted, but in the case of ethyl alcohol, the reaction temperature may be 170–190° C, and the pressure 13–16 atmospheres. The product in this case is ethylene glycol monoethyl ether. The range of products is described generically as glycol ethers.

The monoethers are the most important products, but the reaction normally provides a proportion of di- and triethers, which are also separated for a range of industrial uses. A mass of related products are made on the commercial scale, but the most important are the methyl, ethyl and n-butyl monoethers of ethylene glycol. These are high boiling solvents with many applications, particularly in the surface coatings industries.

$$C_2H_5OH + \underset{\diagdown\,O\,\diagup}{CH_2—CH_2} \rightarrow \underset{\text{ethylene glycol monoethyl ether}}{C_2H_5OCH_2CH_2OH}$$

The free hydroxyl group can be esterified. Some of the acetate esters are also of considerable importance in the surface coatings field.

$$\underset{\text{ethylene glycol monoethyl ether}}{C_2H_5OCH_2CH_2OH} + \underset{\text{acetic acid}}{CH_3COOH} \rightarrow \underset{\text{ethylene glycol monoethyl ether acetate}}{C_2H_5OCH_2CH_2OCOCH_3}$$

Condensation products of ethylene oxide with higher alcohols and substituted phenols are detergent products of the non-ionic type. The most important products are those derived from the condensation of 8–15 mols of ethylene oxide with each mol of alkyl phenol. Octyl, nonyl and dodecyl phenols are the most important in practice. Ethylene oxide is added to the alkyl phenol, using sodium acetate or sodium hydroxide as a catalyst, at such a rate as will keep the temperature at about 200° C. The pressure during this addition is kept at 2–2·5 atmospheres. The condensation products have important applications as detergents and wetting agents in the industrial field, and also as household liquid detergents.

Ethylene oxide will react with ammonia to give a mixture of ethanolamines.

$$\underset{\diagdown\,O\,\diagup}{CH_2—CH_2} + NH_3 \rightarrow \underset{\text{monoethanolamine}}{NH_2CH_2CH_2OH}$$

$$NH_2CH_2CH_2OH + \underset{\diagdown\,O\,\diagup}{CH_2—CH_2} \rightarrow \underset{\text{diethanolamine}}{NH(CH_2CH_2OH)_2}$$

$$NH(CH_2CH_2OH)_2 + \underset{\diagdown\,O\,\diagup}{CH_2—CH_2} \rightarrow \underset{\text{triethanolamine}}{N(CH_2CH_2OH)_3}$$

The exothermic reaction takes place under conditions which may be varied according to the relative requirement of the individual

amines. An excess of ammonia is used. The greater the excess, the higher the proportion of monoethanolamine in the final mixture. Temperature and pressure also have some influence on the product ratio. Pressure may vary from atmospheric to 100 atmospheres, and temperature from 30 to 270° C. Using 30–40° C and a pressure of 1·5 atmospheres, the reaction of ammonia and ethylene oxide in a 10 : 1 mol ratio will yield 75 per cent monoethanolamine, 21 per cent diethanolamine and 4 per cent triethanolamine. Using equimolar proportions under the same conditions, the respective proportions become 12, 23 and 65 per cent. Where triethanolamine is the desired product and low ammonia/ethylene oxide mol ratios are consequently used, some carbon dioxide may be required as a diluent, to suppress ether formation. Alternatively the mono- or diamine can be recycled to repress its proportion in the product mixture. The usual separation by distillation in a multicolumn complex is carried out. Ammonia is stripped off the amine mixture and recycled to the reaction.

The necessity for flexibility in the balance of ethanolamines produced arises from the fact that the relative requirements have been subjected to a good deal of change. Both mono- and diethanolamine are used as absorbents for the removal of acid gases (hydrogen sulphide, carbon dioxide) from gas streams. Other applications exist as chemical intermediates and in the detergent and textile industries. Triethanolamine is widely used in cosmetic and toilet preparations. Their uses stem in many cases from their characteristics as mildly alkaline products.

The only other application of ethylene oxide of major significance today is in the production of acrylonitrile. This is an alternative to the acetylene route already discussed. The first stage of this process is the reaction between ethylene oxide and hydrogen cyanide.

$$\underset{\diagdown\,O\,\diagup}{CH_2—CH_2} + HCN \rightarrow \underset{\text{ethylene cyanohydrin}}{HOCH_2CH_2CN}$$

This production of ethylene cyanohydrin is an exothermic reaction, normally taking place in the presence of a basic catalyst such as diethylamine. The reaction temperature of this batch operation is 55–60° C. The alkaline mixture is neutralized and ethylene cyanohydrin separated by distillation. The second stage may involve passing ethylene cyanohydrin continuously over a dehydration

catalyst such as activated alumina. This is a vapour phase reaction carried out at 300° C. Alternatively, a liquid phase operation may be conducted at 200° C in the presence of a catalyst such as magnesium carbonate.

$$\underset{\text{ethylene cyanohydrin}}{HOCH_2CH_2CN} \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN} + H_2O$$

This was the earliest commercial route to acrylonitrile and it is still practised on a substantial scale.

Polyethylene

Polyethylene, in its various forms, is one of the major achievements in the field of petroleum chemicals.

The original polyethylene, 'high pressure' or 'low density' polyethylene, came from an accidental discovery in 1933. In two respects the exploitation of the discovery required important technological developments. The ethylene used for high pressure polyethylene required to be purified to an extent not before attempted. In addition the operation of an industrial process at the pressure required for this reaction posed many design problems. The ethylene is purified to about 99·9 per cent volume, and mixed with 600 parts per million of oxygen. The mixture is compressed to 1,500–2,500 atmospheres. The temperature in the reactor may vary according to requirements from 100–300° C, but in any particular operation is kept constant. The unreacted ethylene is separated from polyethylene in a separator in which the polymer is in the form of a viscous liquid. This liquid is chilled solid, and is run through a chopper to yield polyethylene flakes. This operation is known as mass polymerization.

Alternatively, solvent polymerization may be used. In this case the reaction is typically carried out at 1,000 atmospheres in the presence of an aromatic hydrocarbon. Purified ethylene with 20 parts per million of oxygen is dissolved in a benzene–water mixture at 1,000 atmospheres and 200° C. The mixture passes to the reactor, and the oxygen catalyst concentration is maintained by adding water containing 100 parts per million of oxygen. The reactor effluent passes to a separator, and the liquid phase is subsequently distilled to remove the solvent from the polymer.

Variations in pressure, temperature and other conditions will

modify the molecular weight, and hence the properties, of the finished product. High pressure polyethylene has a molecular weight ranging between 10,000 and 40,000 and a typical density of 0·92 gm/c.c.

In the middle 1950's, the commercial development of a different type of polyethylene began, based on Ziegler catalysts. This polyethylene, described as a 'low pressure' or 'high density' product (typical density 0·96 gm/c.c.), has appreciably different properties from the conventional high pressure product. In particular it is more rigid, and has a higher softening temperature. These two types of polyethylene are, therefore, to a large extent complementary rather than competitive.

A Ziegler catalyst system is complex and variable. For the production of low pressure polyethylene, a typical combination is triethylaluminium reacted with titanium tetrachloride.

The catalyst contacts the ethylene stream in an unreactive hydrocarbon medium. The titanium trichloride, which is one of the products of the complex catalyst reaction, is insoluble in the hydrocarbon, and is present as a dispersed solid phase. The purified ethylene has appreciable solubility in the hydrocarbon. Typical polymerization conditions are 6–7 atmospheres pressure and 100–170° C.

The separation and purification of the polymer presents a problem in this case, because any traces of catalyst left in the product will render it unacceptable. It is possible to use a number of different purification treatments. The solvent may be flashed off the polymer, which is then treated with water to kill the catalyst. Alternatively, the catalyst may be deactivated with alcohol. The polymer is then filtered from the solvent mixture and dried. The dry polymer is extruded into strands, cooled, and cut into pellets.

A third process for polyethylene manufacture has also been developed to the commercial stage in the past few years. This is the Phillips low pressure process. This also requires pure ethylene, which is absorbed as a 5–7 per cent solution in xylene. The solution is pumped to a reactor, where it contacts a catalyst (molybdenum or chromium oxides on alumina) at 30–100 atmospheres pressure and 175–260° C. The reaction products pass to a separator, where ethylene is drawn off and recycled. The hot polymer solution is filtered to remove catalyst, chilled to precipitate polyethylene, and then filtered again.

A variation of this process uses nickel on activated carbon as a catalyst, with a calcium hydride promoter. Ethylene at 65 atmospheres pressure is reacted in a benzene slurry at temperatures ranging from 20–250° C.

Whilst the Phillips process is called a low pressure process, it really uses intermediate pressure in comparison with the other two processes. The effect of this range of processes is to give a wide variety of polyethylenes with a spread of such properties as density, softening point and rigidity. The range of properties is further supplemented by the development of blends and finishing processes to meet specialized requirements.

Statistics for the production and usage of polyethylene are conveniently subdivided between the high pressure and low pressure products as follows:

HIGH PRESSURE POLYETHYLENE IN 1960

	U.S.A.	*United Kingdom*
Production (tons)	500,000	105,000
Home consumption (tons)	320,000	58,000
Usage:		
Injection moulding	12%	32%
Blow moulding	2%	7%
Film and sheet	48%	27%
Cables }	19%	11%
Piping }		15%
Miscellaneous	19%	8%

LOW PRESSURE POLYETHYLENE IN 1960

	U.S.A.	*United Kingdom*
Production (tons)	100,000	1,000
Home consumption (tons)	67,000	7,000
Usage:		
Injection moulding	53%	60%
Blow moulding	23%	10%
Monofilament }	13%	15%
Piping }		10%
Miscellaneous	11%	5%

Figures from a different source (quoted in the section on the plastics industry) give a slightly different picture for polyethylene in the United Kingdom in 1960–61.

The arrival of polyethylene has wrought a revolution in the fields of packaging and flexible containers. A number of the applications for polyethylene derive from its outstanding electrical properties. The newer 'high density' grades are entering the associated field of semi-rigid mouldings, where they are likely to offer competition in some cases to the polystyrene resins.

Styrene

There are a number of theoretically possible routes to styrene (vinyl benzene). One of them has achieved an outstanding importance, and two others have minor commercial significance.

The production of styrene via acetophenone is in commercial operation on a limited scale. The first step is the alkylation of benzene with ethylene to give ethyl benzene, which is considered in more detail below. Ethyl benzene is oxidized in the liquid phase with air to acetophenone. The acetophenone is then hydrogenated, in the presence of a copper–chromium–iron catalyst to phenyl ethyl alcohol. The latter is dehydrated over a titania catalyst to styrene.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{ethylene}}{C_2H_4} \rightarrow \underset{\text{ethyl benzene}}{C_6H_5CH_2CH_3}$$

$$C_6H_5CH_2CH_3 + O_2 \rightarrow \underset{\text{acetophenone}}{C_6H_5COCH_3} + H_2O$$

$$C_6H_5COCH_3 + H_2 \rightarrow \underset{\substack{\text{phenyl ethyl}\\ \text{alcohol}}}{C_6H_5CHOHCH_3}$$

$$C_6H_5CHOHCH_3 \rightarrow \underset{\text{styrene}}{C_6H_5CH{=}CH_2} + H_2O$$

The Alkar process, which is not yet fully commercially developed, is designed to produce ethyl benzene from by-product gas streams with a relatively low proportion of ethylene. A further development in ethyl benzene production in the U.S.A. has been the use of superfractionation techniques to separate ethyl benzene from aromatic concentrates such as may be derived from catalytic reforming.

The production of ethyl benzene is commonly achieved by the alkylation of dry 99 per cent benzene using a 95 per cent ethylene

stream in contact with a catalyst of aluminium chloride or phosphoric acid. The most common operation is carried out in the liquid phase as a Friedel–Crafts reaction using aluminium chloride. Reaction conditions in such a case are 85–95° C and a slightly elevated pressure. The ratio of ethylene to benzene (0·6 mol ethylene to 1 mol benzene) is chosen to give the maximum yield of monoethyl benzene, and to minimize production of higher alkyl benzenes. A small quantity of ethyl chloride is associated with the ethylene feed. The ethyl chloride breaks down into ethylene and hydrogen chloride, and the latter acts as a promoter to the aluminium chloride catalyst.

The products of the alkylation reaction are washed with sodium hydroxide solution and water. The catalyst then separates in the aqueous layer. The remaining mixture contains unreacted benzene, monoethyl benzene, and a complex mixture of higher alkyl benzenes and tar. This is separated in a series of distillation columns. Benzene is taken overhead from the first column, and recycled to the alkylator. Monoethyl benzene is the overhead product of the second column, operated at 200 mm Hg. The third column operates at 40 mm Hg. The bottom product of the third column is the crude 'tar'. The overhead product is a mixture of polyethyl benzenes, which may either be treated in a high temperature dealkylator at about 200° C (producing benzene and ethyl benzene which are returned to the system) or may be returned to the alkylator, where it is dealkylated, and suppresses the formation of fresh polyethyl benzenes, by virtue of the equilibrium of the reaction (this latter technique may be applied with the aluminium chloride catalyst, but not with phosphoric acid).

The next step is the dehydrogenation of ethyl benzene to styrene.

$$\underset{\text{ethyl benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{styrene}}{C_6H_5CH{=}CH_2} + H_2$$

It is a strongly endothermic reaction, accompanied by an increase in volume. Optimum conditions will, therefore, include a high temperature and low pressure. The reaction temperature, designed to achieve a satisfactory reaction rate, but to avoid excess degradation, is between 600–660° C. The reduction in pressure is achieved in practice by the use of superheated steam (2·6 lb/lb ethyl benzene) as a diluent. The catalyst used is metallic oxide in character. One alternative is a mixture of magnesium and iron oxides, and the other zinc oxide. These are in the form of hard pellets. The reaction products are first cooled against incoming ethyl benzene, and then by steam in heat exchangers. A spray cooler lowers the product temperature to 105° C, and condenses out tars. The fully condensed reaction product typically contains styrene 35–37 per cent weight, ethyl benzene 59–61 per cent, toluene 1–2 per cent, benzene 0·5–2 per cent and tars 0·2–0·5 per cent.

The gas stream, consisting of impure hydrogen, may be used as fuel or for other chemical reactions.

The separation problems arising from the composition of the reaction product are complex, and involve distillation at fairly high vacuum (i.e. a very much reduced pressure). It is necessary, as a preliminary, to dissolve a small proportion of sulphur in the crude styrene to act as a polymerization inhibitor. In the first column, or dual-column system, benzene and toluene are taken overhead and separated. The benzene is returned to the ethyl benzene alkylator. The separation of styrene and ethyl benzene involves a two- or three-column system operated under vacuum. Ethyl benzene is taken overhead from the first or second column, according to the system used. The final styrene column provides pure styrene as the top product, and a tarry residue at the bottom. The residue may be burned, or passed to a styrene recovery system.

Styrene is one of the most important products in the petroleum chemical field. The annual capacity for styrene production in the United Kingdom had reached 68,000 long tons by the end of 1960, compared with a production in the U.S.A. of 701,000 long tons in 1959, and 780,000 in 1960.

The breakdown of styrene consumption in the U.S.A. in 1960 has been quoted as follows:

Polystyrene (general purpose)	20%
Other styrene polymer resins	27·5%
Synthetic rubber (SBR)	29%
Protective coatings	5·5%
Polyesters	3%
Exports	7%
Miscellaneous	8%

The biggest single use for styrene is still the manufacture of polystyrene, which in 1959 was produced to the extent of 37,500 tons in

the United Kingdom, and 416,000 tons in the U.S.A. The usage of polystyrene in the United Kingdom in 1959 was as follows:

Refrigerator parts	23%
Packaging	16%
Electrical, radio and gramophone	15%
Housewares	14%
Toys	12%
Sheet uses (other than refrigerators)	8%
Shoe heels	5%
Expanded materials	3%
Wall tiles	1%
Miscellaneous	3%

It may be of interest to compare this with the somewhat less detailed table in the section on the plastics industry, referring to 1960 conditions in the United Kingdom.

Polystyrene can be made in a number of different ways. Continuous mass polymerization gives a product of excellent clarity but less satisfactory moulding properties. Solution or suspension polymerization gives much better control of molecular weight, and hence improved moulding qualities, but trace impurities tend to impair the clarity.

Polystyrene itself tends to be brittle, and much attention has been paid to the production of 'high impact' grades. This is normally effected by incorporating 10–12 per cent of natural or synthetic rubber into polystyrene.

Modified polymers are produced by the co-polymerization of styrene with such monomers as acrylonitrile or methyl methacrylate. Such co-polymers are designed to combine the desirable moulding properties and cheapness of polystyrene, with specific requirements for a variety of uses. This is one of the faster moving sectors of the styrene market.

By the incorporation of about 10 per cent of a volatile hydrocarbon, such as pentane or butane, into polystyrene granules or beads, the beads can be expanded into a low density block or board. This material has exceptionally good thermal insulating properties. The beads can be treated with a flame-retarding compound, which will eliminate the hazard of inflammability of the finished board. This is obviously important where the insulating board is to be used in housing construction.

The other major application of styrene in the production of the standard (SBR) type of synthetic rubber is considered in more detail later.

Ethyl Chloride

Ethylene is the major source of ethyl chloride, although some production is derived from both ethane and ethyl alcohol. The reaction is a straightforward hydrochlorination.

$$CH_2{=}CH_2 + HCl \rightarrow \underset{\text{ethyl chloride}}{CH_3CH_2Cl}$$

The reaction may proceed in the vapour phase, usually at temperatures of 130–250° C, in the presence of aluminium chloride as catalyst. Alternatively, at 35–40° C, and pressures sufficiently above atmospheric to maintain the reaction products in the liquid phase, the reaction will proceed in the liquid phase, using ethylene dichloride (possibly with some ethyl chloride) as a solvent, and aluminium chloride as catalyst. The heated products are fed into a column or flash drum, where ethyl chloride is separated from the less volatile polymer by-products. The ethyl chloride is then purified by fractionation.

By far the greatest proportion of ethyl chloride goes into tetraethyl lead, for the improvement of gasoline quality. It has some other applications as a refrigerant, anaesthetic, etc. The production in the U.S.A. amounted to 600 million lb in 1960.

Ethylene Dichloride

The reaction between chlorine and ethylene is an exothermic addition reaction.

$$CH_2{=}CH_2 + Cl_2 \rightarrow \underset{\text{ethylene dichloride}}{CH_2ClCH_2Cl}$$

The reaction will take place either in the vapour or liquid phase. There is no vapour phase reaction, in the absence of a catalyst, at moderate temperatures. Using a catalyst, comprising a metal chloride on an inert support, a dilute ethylene stream (e.g. in coke oven gas) has been reacted to produce ethylene dichloride.

Where a concentrated ethylene stream is available (which is commonly the case with petroleum-based gas streams) it is preferable to conduct the reaction in the liquid phase. This again uses a metal chloride catalyst, with a temperature up to 50° C, and the pressure atmospheric or slightly raised. In practice, ethylene dichloride or ethylene dibromide may be used as solvents in the reaction zone. Temperature control is important, to minimize the production of more highly chlorinated products. The liquid products from the reactor are washed with dilute sodium hydroxide to remove hydrochloric acid. Ethylene dichloride is purified by distillation.

An alternative process involves bubbling the chlorine through ethylene dibromide, and passing the mixed vapours into a chlorinating tower at 40–50° C. The chlorine there meets an ethylene stream. The reaction products are taken to a partial condenser at 85° C, where the ethylene dibromide liquefies and is recycled. The ethylene dichloride vapour is introduced to a fractionating tower, and separated as a pure product.

A certain proportion of ethylene dichloride manufacture arises from its recovery as a by-product in the chlorohydrin route to ethylene oxide.

There are two substantial uses for ethylene dichloride. Firstly, it is used as a component in tetraethyl lead fluid for gasoline improvement. Secondly, it is one of the major raw materials for vinyl chloride. In 1960, approximately 46 per cent of U.S.A. vinyl chloride, or about 460 million lb, was derived from this source.

The production of vinyl chloride involves the dehydrochlorination of ethylene dichloride.

$$\underset{\text{ethylene dichloride}}{CH_2ClCH_2Cl} \rightarrow \underset{\text{vinyl chloride}}{CH_2{=}CHCl} + HCl$$

This dehydrochlorination may be achieved either by pyrolysis, or by treatment with sodium hydroxide.

The pyrolysis process passes ethylene dichloride at 480–500° C and 3 atmospheres pressure over a catalyst of pumice or kaolin. The exit gases are quenched in a stream of condensed unreacted ethylene dichloride. Uncondensable gases are scrubbed with water to recover hydrogen chloride. Vinyl chloride is recovered from the liquid mixture by distillation under 5 atmospheres pressure, and is purified by redistillation.

An alternative process requires ethylene dichloride to be heated in the presence of sodium hydroxide.

$$CH_2ClCH_2Cl + NaOH \rightarrow CH_2{=}CHCl + NaCl + H_2O$$

The reaction takes place at 10 atmospheres pressure and 140–150° C. Products overflowing from the reactor are cooled and pumped to a distillation column operating under pressure. From the column bottoms unreacted ethylene dichloride is recovered and recycled.

The production of ethylene dichloride in the U.S.A. in 1960 approximated to 1,200 million lb.

Ethylene Dibromide

This process is analogous to that producing ethylene dichloride, and is the only major industrial use for bromine (commonly recovered from sea water).

The addition of bromine to ethylene gives ethylene dibromide.

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$

The process conditions are similar in principle to those for ethylene dichloride.

The major application for ethylene dibromide is in conjunction with ethylene dichloride in the preparation of tetraethyl lead fluid as a gasoline additive. Additional applications include soil fumigation (e.g. for nematode control) and for grain fumigation.

Acetaldehyde (Wacker process)

The major current commercial processes for acetaldehyde have already been considered. The Wacker process, now under development, looks like being a vigorous competitor in this important field. A variety of alternatives are being studied.

The oxidation of ethylene to acetaldehyde involves the use of palladium chloride as catalyst. The basic reactions involving palladium chloride are:

$$CH_2{=}CH_2 + PdCl_2 + H_2O \rightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

$$Pd + 2HCl + \tfrac{1}{2}O_2 \rightarrow PdCl_2 + H_2O$$

The first reaction is rapid and the second relatively slow. Cuprous

chloride is therefore introduced, in effect as a promoter for the second of the above reactions

$$2CuCl_2 + Pd \rightarrow 2CuCl + PdCl_2$$
$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O$$

The net reaction and regeneration steps using cuprous chloride as a promoter may be expressed as follows, leaving the palladium chloride unchanged.

$$CH_2{=}CH_2 + 2CuCl_2 + H_2O \xrightarrow{PdCl_2} \underset{\text{acetaldehyde}}{CH_3CHO} + 2HCl + 2CuCl$$
$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

The process may be carried out as a one-stage operation in the liquid phase, for both reaction and regeneration. This requires a pure ethylene stream for the reaction, and oxygen for the regeneration.

The two-stage operation, also in the liquid phase, can employ any ethylene-rich stream in the reaction stage, and air oxidation in the regeneration stage. In each case the reaction takes place at moderate temperature and slightly elevated pressure.

Alternative processes to acetaldehyde either involve an indirect derivation from ethylene via ethyl alcohol, or the use of acetylene, which is inherently a more expensive raw material than ethylene. There is an obvious potential economic advantage in a direct high yielding derivation from ethylene. This is another illustration of a major guiding principle (the tendency to simplify synthesis processes) in modern industrial chemistry.

On the strength of the prospects of this process, it has been postulated as a basis for an alternative route to acrylonitrile, which may be competitive with the existing routes from acetylene and ethylene oxide. The proposed process treats acetaldehyde with hydrogen cyanide at 10–20° C to give lactonitrile.

$$CH_3CHO + HCN \rightarrow \underset{\text{lactonitrile}}{CH_3CHOHCN}$$

Lactonitrile has then to be dehydrated to acrylonitrile. This may be accomplished at high temperature (600–700° C) in the presence of phosphoric acid. The reaction is followed immediately by quenching with 30 per cent phosphoric acid.

$$\underset{\text{lactonitrile}}{CH_3CHOHCN} \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN} + H_2O$$

The overall yield of acrylonitrile from ethylene is expected to be much higher by this method than via ethylene oxide.

Although it would be premature to say that all the practical problems of these processes have been fully worked out, they possess sufficient economic promise to be actively developed to the commercial stage. Several production units for acetaldehyde are under construction at the moment of writing.

Ethylene-Propylene Rubbers (EPR)

The concept of producing commercially acceptable rubbers by the co-polymerization of ethylene and propylene has obvious attractions. Ethylene and propylene are both economical monomers, and, if a reasonable process can be devised to offer a product of acceptable quality, a highly attractive project should result. A practical point is that the ethylene–propylene rubbers have a lower density than most competitive materials. Since many rubber products (such as tyres) involve a specific volume of rubber, the same dimensions can be produced with a reduced weight, and, presumably, lower raw material cost.

Present developments stem from the same family of Ziegler catalysts as is used for low pressure polyethylene.

Commercial processes are in course of development although full-scale production has not commenced at the time of writing.

The properties of the ethylene-propylene rubbers present some difficulties from the point of view of subsequent processing. The polymer molecule, as with polyethylene, contains at most two double bonds in an extremely large molecule. In the polymerization, the chain structure takes the place of the double bonds.

$$CH_2{=}CH_2 \xrightarrow{\text{polymerization}} {-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}$$

The molecule is, therefore, for all practical purposes, saturated. Vulcanization using sulphur, in the ordinary way, is therefore impossible. It is possible to apply the less familiar peroxide vulcanization.

It is commercially desirable to modify the molecule so that normal vulcanization techniques can be employed. Two main possibilities may be considered. Additional double bonds may be introduced into the polymer molecule by co-polymerizing with a small proportion of

dienes (as is done with butyl rubber). It is alternatively possible to subject the polymer to a substitution reaction, such as chlorination, so that there are additional points of chemical activity along the molecule, which will respond to vulcanization techniques and produce the desired cross linkage effect.

Once this major problem has been overcome, it will still be necessary to establish techniques for using the rubber in such specialized processes as tyre manufacture. Ethylene-propylene rubbers are lacking, for instance, in 'tack' (or bonding power), a characteristic desirable for tyre rubbers. Such difficulties can usually be overcome, but always at a cost.

Ethylene-propylene rubbers do not fit neatly into any of the existing categories. They probably have more in common with butyl rubber than any other type, and are more likely to replace general purpose synthetic rubbers (SBR) than natural rubber. It is, however, too early to give an authoritative technological or commercial assessment.

Chapter 8

Propylene Derivatives

The usage of propylene in the production of chemicals is indicated by the following tables.

The consumption of propylene for chemical production in the U.S.A. has developed as follows (in millions of lb).

1950	*1955*	*1958*	*1960*	*1965 (est.)*
1,100	1,400	1,950	2,500	3,500

The breakdown of consumption in the U.S.A. is as follows (1959):

Isopropyl alcohol	42·7%
Propylene tetramer	29·1%
Propylene oxide	10·5%
Propylene trimer	6·1%
Cumene	3·6%
Glycerine	3·3%
Oxo chemicals	3·3%
Polypropylene	0·9%
Epoxy resins	0·5%

Propylene consumption in France, also for 1959, is broken down as follows:

	million lb.
Propylene tetramer	60
Cumene	55
Isopropyl alcohol	50
Propylene trimer	10
Propylene oxide	10
Miscellaneous	10
	195

For the United Kingdom, such a composite breakdown is not easily available. Current isopropyl alcohol production is a little over 100,000 long tons/year (which would involve the consumption of approximately 80 per cent of this tonnage of propylene) of which two-thirds is converted to acetone. The capacity for propylene for

chemical use in the United Kingdom has been estimated as currently reaching approximately 280,000 metric tons/year.

Canada's consumption of propylene for chemical use reached over 31,000 tons in 1959.

In the U.S.A. there has been little requirement to undertake special cracking operations for propylene manufacture. Propylene is obtainable in large quantities from refinery cracking operations, and this, supplemented by some additional propylene obtained as a by-product from the cracking of propane to ethylene, has been sufficient to meet the need.

It is relatively simple to isolate a C_3 fraction from a mixed gas stream, and, until the advent of polypropylene, a C_3 stream, frequently containing a substantial proportion of propane, was a perfectly suitable feedstock for chemical conversion, with the exception of the hot chlorination process to allyl chloride. The value of propylene as a chemical raw material has therefore been geared to its 'alternative use value' in the petroleum field (i.e. as fuel or as liquefied petroleum gas). It is therefore one of the most economical of the olefin feedstocks.

In Europe, propylene is produced, alongside other olefins, in naphtha cracking operations of petroleum chemical complexes. Here again, refinery propylene is commonly available as an alternative raw material. The availability of refinery propylene, therefore, sets the standard of propylene values on the basis of the stern facts of commercial competition. The placing of differential values on the different olefinic gas streams produced in the same naphtha cracking operation may seem illogical, but is inevitable in the light of the current European raw material position.

Isopropyl Alcohol and its Derivatives

This family of products was one of the first groups of petroleum chemicals to be commercially developed.

Isopropyl alcohol is produced from propylene by hydration. This hydration is most commonly effected indirectly by a concentration–dilution process, involving absorption in sulphuric acid, and subsequent hydrolysis.

$$CH_3CH{=}CH_2 + H_2SO_4 \rightarrow CH_3CH(OSO_3H)CH_3$$
$$CH_3CH(OSO_3H)CH_3 + H_2O \rightarrow CH_3CH(OH)CH_3 + H_2SO_4$$

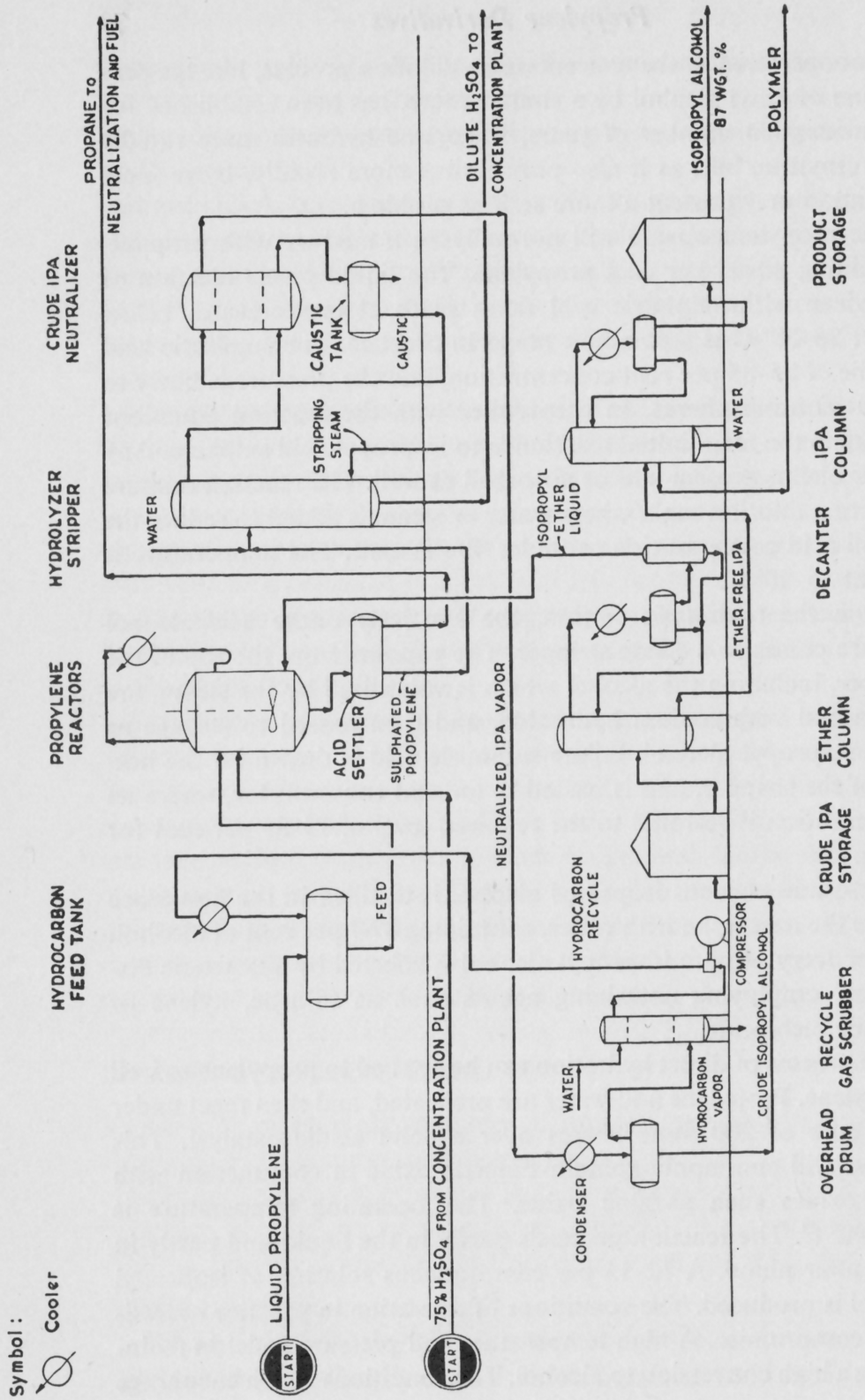
This operation of the concentration–dilution process, like the production of ethyl alcohol by a similar route, has been established for a considerable number of years. Propylene hydrates more rapidly than ethylene, but, as it also polymerizes more rapidly, by-product formation may present a more serious problem.

The propylene stream will normally be a mixture with propane, containing 40–95 per cent propylene. The liquid phase reaction of propylene with sulphuric acid takes place at temperatures below 40° C. 20–30° C is a common range in practice. The sulphuric acid may be of 75–85 per cent concentration, and the pressure is likely to be 20–30 atmospheres. In accordance with the reaction equations indicated, the main initial reaction is to isopropyl acid sulphate. Any higher olefins present will be absorbed as well. The reaction mixture flows to a dilution tank, where water or steam is added to reduce the overall acid concentration to under 40 per cent. The temperature is kept at 35–40° C.

From the hydrolysis section, the relatively dilute acid/alcohol mixture passes to a steam stripper. The vapours from the top of the stripper, including the alcohol which is volatilized by the steam, are neutralized with sodium hydroxide, and then passed to storage as crude isopropyl alcohol. Dilute sulphuric acid is drawn off the bottom of the stripper, and is passed to an acid concentrator, where its concentration is restored to the required level of 75–85 per cent for re-use.

The crude aqueous isopropyl alcohol is distilled in the first place to give the azeotrope with water, containing 87·7 per cent of alcohol. The recovery of pure isopropyl alcohol is effected by azeotropic distillation, employing entraining agents such as toluene, xylene or ethylene dichloride.

The process of direct hydration can be applied to propylene as well as ethylene. Propylene and water are preheated, and then react under a pressure of 200 atmospheres over a solid acidic catalyst. This catalyst will commonly contain tungstic oxide in conjunction with other oxides such as zinc oxide. The operating temperature is 200–240° C. The reaction proceeds partly in the liquid and partly in the vapour phase. A 12–15 per cent aqueous solution of isopropyl alcohol is produced. The conditions of operation in practice necessitate a compromise. A high temperature and pressure assist in maintaining a high conversion to alcohol. The conditions which encourage



ISOPROPYL ALCOHOL FROM PROPYLENE BY CONCENTRATION–DILUTION PROCESS
(Design by Stone and Webster Engineering Corporation)

the formation of unwanted polymer include also high temperature and pressure, as well as a low water/propylene ratio.

Earlier production of isopropyl alcohol was on the basis of the hydrogenation of acetone, where the acetone was derived from fermentation. In view of the fact that petroleum-based acetone, made from isopropyl alcohol, can compete favourably with fermentation acetone, it is obvious that the production of isopropyl alcohol from fermentation acetone is no longer economic.

The main usage of isopropyl alcohol is in the production of acetone, where the 87·7 per cent alcohol azeotrope is normally employed as raw material. Anhydrous and absolute grades of isopropyl alcohol have applications as solvents, gasoline additives, etc. A development of considerable potential significance is the commercial application of the oxidation process, whereby hydrogen peroxide is obtained from isopropyl alcohol. This is discussed separately on page 88.

As has been pointed out, the main commercial application of isopropyl alcohol is its dehydrogenation to acetone (some 60 per cent of isopropyl alcohol in the U.S.A. is so consumed). This is likewise the major source of acetone, although there are a number of competitive sources. The only non-petroleum basis is the fermentation process commonly based on starch or molasses, to produce n-butyl alcohol and acetone. Whilst this is still operated commercially, it has been largely superseded. Amongst petroleum chemical processes, acetone is a co-product with phenol produced from propylene via cumene (page 89), with hydrogen peroxide by oxidation of isopropyl alcohol (page 88), and with allyl alcohol in the newly developed alternative glycerine synthesis (page 85).

Vaporized isopropyl alcohol, at 500° C and about 3 atmospheres, on passing over a brass or copper catalyst is dehydrogenated to acetone.

$$(CH_3)_2CHOH \rightarrow CH_3COCH_3 + H_2$$

Isopropyl alcohol and acetone are condensed from the reaction gas stream, and separated by fractionation. The hydrogen stream is of value for other chemical reactions, including the frequently associated hydrogenation of mesityl oxide to methyl isobutyl ketone.

There are a number of variations of this widely used process. It can be modified to a combined oxidation–dehydrogenation reaction, passing air with the isopropyl alcohol over a silver or copper catalyst.

The major importance of acetone, as an industrial product, is indicated by the scale of production. In 1960, production in the U.S.A. was about 340,000 long tons, compared with a capacity in the United Kingdom of 90,000 long tons. The basis of U.S. consumption has been quoted as follows:

Derivative solvents	
Methyl isobutyl ketone	21%
Methyl isobutyl carbinol	10%
Others	12%
Methyl methacrylate	14%
Drugs and miscellaneous chemicals	12%
Solvent uses	
Paint, varnish, lacquer	10%
Cellulose acetate	5%
Acetylene	4%
Miscellaneous	11%
Exports	1%

Apart from the major solvent applications, acetone is an important chemical intermediate for such products as methyl methacrylate and cellulose acetate via acetic anhydride. Probably its major single usage is concerned with the group of solvents represented by the synthesis chain from acetone to methyl isobutyl carbinol, which commonly forms one integrated series of units, alongside the isopropyl alcohol and acetone production units. The important solvent applications include a variety of uses in the paint and lacquer field, the carrier solvent for acetylene in cylinders, and use as a dope for cellulose acetate spinning.

The first step in this series of reactions is a condensation reaction of acetone to diacetone alcohol. Acetone is refrigerated to about 0–5° C and passed through a column packed with soda lime.

$$\underset{\text{acetone}}{CH_3COCH_3} + CH_3COCH_3 \rightarrow \underset{\text{diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3}$$

Diacetone alcohol has some solvent applications, and is a component of certain brake fluids. It is mostly used as a chemical intermediate. An incidental reaction of some commercial significance is its hydrogenation to hexylene glycol, which is also a brake fluid component. The reaction takes place over a Raney nickel catalyst (this is specially prepared nickel in a finely divided form which is an exceedingly active catalyst for many medium-pressure hydrogenation reactions), at 35 atmospheres pressure and 70–80° C.

$$\underset{\text{diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3} \xrightarrow{+H_2} \underset{\substack{\text{hexylene glycol}\\(\text{2-methyl-2,4-pentanediol})}}{(CH_3)_2C(OH)CH_2CHOHCH_3}$$

The main stream of diacetone alcohol is directed to the dehydration process forming mesityl oxide.

$$\underset{\text{diacetone alcohol}}{(CH_3)_2C(OH)CH_2COCH_3} \xrightarrow{-H_2O} \underset{\text{mesityl oxide}}{(CH_3)_2C{=}CHCOCH_3}$$

The dehydration takes place at 100–120° C in the presence of an acid such as sulphuric acid. Mesityl oxide has little commercial significance (its somewhat unattractive smell being a disadvantage in the development of its solvent applications) except as an intermediate in the production of methyl isobutyl ketone. This hydrogenation reaction takes place at 150–200° C, and 3–10 atmospheres pressure, over a copper or nickel catalyst. If the hydrogenation is allowed to proceed further, the main product is methyl isobutyl carbinol. The balance of these two products is therefore kept in adjustment by the ratio of hydrogen to mesityl oxide.

$$\underset{\text{mesityl oxide}}{(CH_3)_2C{=}CHCOCH_3} \xrightarrow{+H_2} \underset{\text{methyl isobutyl ketone}}{(CH_3)_2CHCH_2COCH_3}$$

$$\underset{\text{methyl isobutyl ketone}}{(CH_3)_2CHCH_2COCH_3} \xrightarrow{+H_2} \underset{\text{methyl isobutyl carbinol}}{(CH_3)_2CHCH_2CH(OH)CH_3}$$

Here one can see one of the benefits accruing from an integrated project, since the hydrogen stream obtained from the dehydrogenation of isopropyl alcohol to acetone may be employed in this hydrogenation.

The two hydrogenation products are separated and purified by distillation. They are important solvents in the paint and lacquer trade. Methyl isobutyl carbinol also finds applications in the froth flotation process for the treatment of ores.

Glycerine

The development of a successful commercial process for the synthesis of glycerine is regarded as one of the major achievements in the petroleum chemical field. Glycerine has long been made as a by-product of the soap and fat-splitting industries. As a by-product, it

was subject to wide fluctuations in price and demand. The availability of a synthetic product introduced some stability to the market position.

The first step in the original synthetic glycerine route is the celebrated 'hot chlorination' of propylene. Contrary to the concepts of classical organic chemistry, it is possible, by a choice of reaction conditions, to chlorinate propylene as a substitution reaction, without disruption of the double bond in the propylene molecule.

$$\underset{\text{propylene}}{CH_2{=}CHCH_3} + Cl_2 \rightarrow \underset{\text{allyl chloride}}{CH_2{=}CHCH_2Cl} + HCl$$

Dry propylene is preheated and mixed with chlorine in a propylene/chlorine mol ratio of 4 : 1. The reaction takes place at about 500° C and 2 atmospheres pressure, with a contact time of about 2 seconds.

From the cooled reaction products, propylene and allyl chloride are drawn off in a fractionating column. The crude allyl chloride, taken from the bottom of the column, is distilled in two further columns. Pure allyl chloride is taken overhead from the second of these columns.

Allyl chloride is reacted with pre-formed hypochlorous acid (formed in a separate tower by reacting chlorine and water) to produce a mixture of dichlorohydrins. The reaction takes place at 28° C in the aqueous phase. The effluent from the reactor is sent to a separator, from which the aqueous phase is recycled to the hypochlorous acid tower. The non-aqueous phase passes to another reactor, where the dichlorohydrins are converted almost completely to epichlorohydrin by a reaction with milk of lime.

$$\underset{\substack{\text{allyl}\\\text{chloride}}}{CH_2{=}CHCH_2Cl} + \underset{\substack{\text{hypochlorous}\\\text{acid}}}{HOCl} \rightarrow \underset{\text{dichlorohydrin}}{CH_2OHCHClCH_2Cl}$$

$$2CH_2OHCHClCH_2Cl + Ca(OH)_2 \rightarrow \underset{\text{epichlorohydrin}}{2CH_2{-}CHCH_2Cl\ (\text{O})} + CaCl_2.2H_2O$$

The epichlorohydrin is recovered from this operation as a water azeotrope by steam distillation, and concentrated to 98 per cent by further distillation.

Epichlorohydrin is then hydrolysed with a 10 per cent solution of sodium hydroxide in a stirred reactor at 150° C.

$$\underset{\text{epichlorohydrin}}{CH_2{-}CHCH_2Cl\ (\text{O})} + NaOH + H_2O \rightarrow \underset{\text{glycerine}}{CH_2OHCHOHCH_2OH} + NaCl$$

The glycerine is produced as a dilute solution containing salt. This solution is evaporated, desalted and concentrated to 98 per cent by distillation.

Subsequent to the development of this process, the intermediate product, epichlorohydrin, has achieved significance in its own right as one of the raw materials in the range of epoxy resins. These resins have properties of great value in specialized surface coatings and certain electrical and engineering functions. The normal reaction is between epichlorohydrin and diphenylolpropane (itself produced from phenol and acetone).

Whilst the process outlined has proved entirely successful in operation, it has one fundamentally unsatisfactory feature. This is the requirement of chlorine in the initial reaction, only for it to be wasted as unwanted calcium and sodium chlorides in the later stages. More recent efforts have turned, therefore, to the development of a process which would eliminate this need for chlorine. An obvious starting point for such a route would be the oxidation of propylene. Large-scale investigations over an extended period have culminated in an alternative glycerine process, which is only now achieving its commercial baptism.

The first step is the oxidation of propylene to acrolein in the presence of a solid copper oxide catalyst. Steam is also added to the reaction, and the temperature requires to be closely controlled within the limits of 300–400° C.

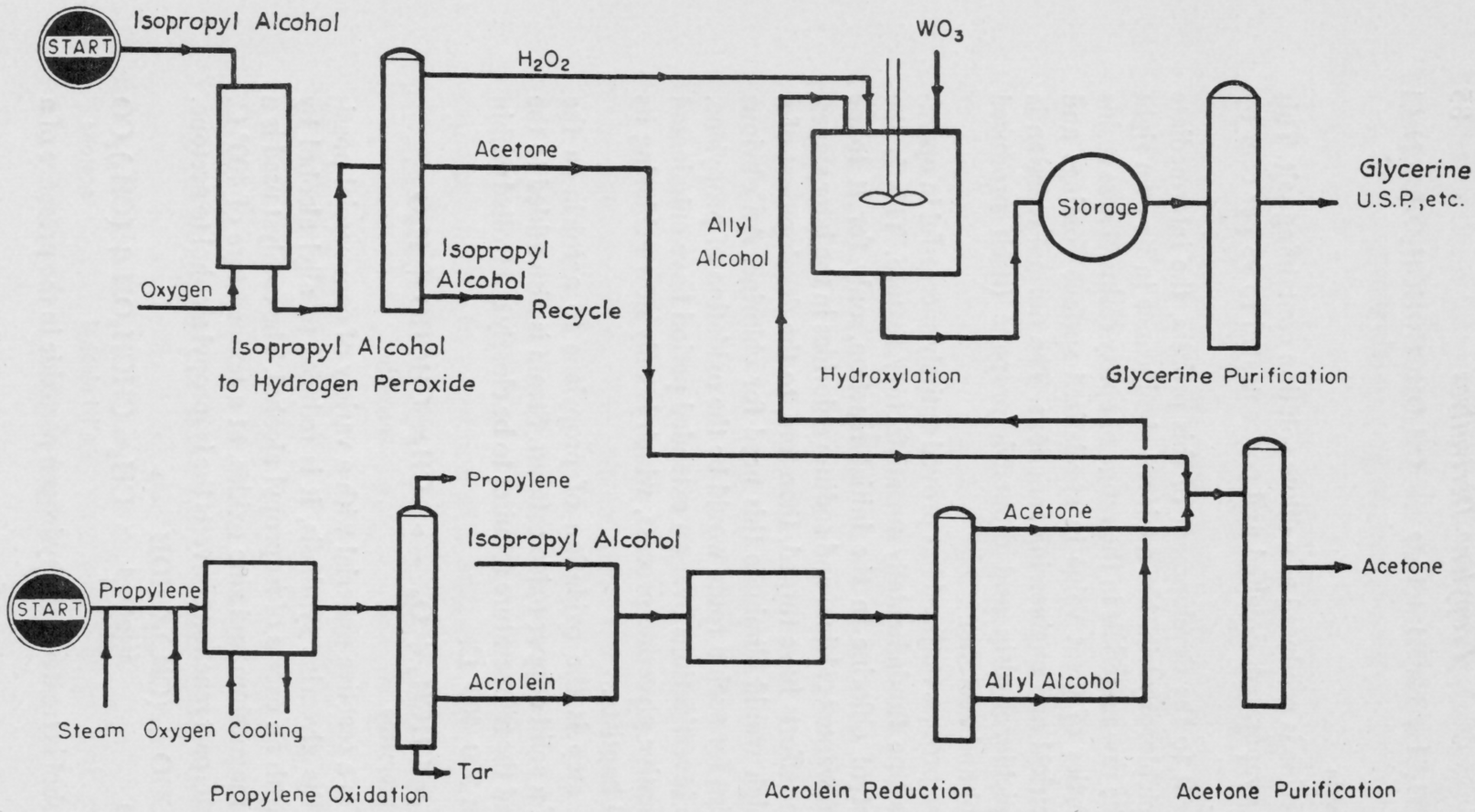
$$\underset{\text{propylene}}{CH_2{=}CHCH_3} + O_2 \rightarrow \underset{\text{acrolein}}{CH_2{=}CHCHO} + H_2O$$

Acrolein is a reactive material with a variety of commercial possibilities. In the glycerine synthesis, it is reduced to allyl alcohol by treating it with an excess of isopropyl alcohol. The catalyst used is a mixture of magnesium and zinc oxides, at a temperature of 400° C.

The counterpart reaction converts the isopropyl alcohol to acetone.

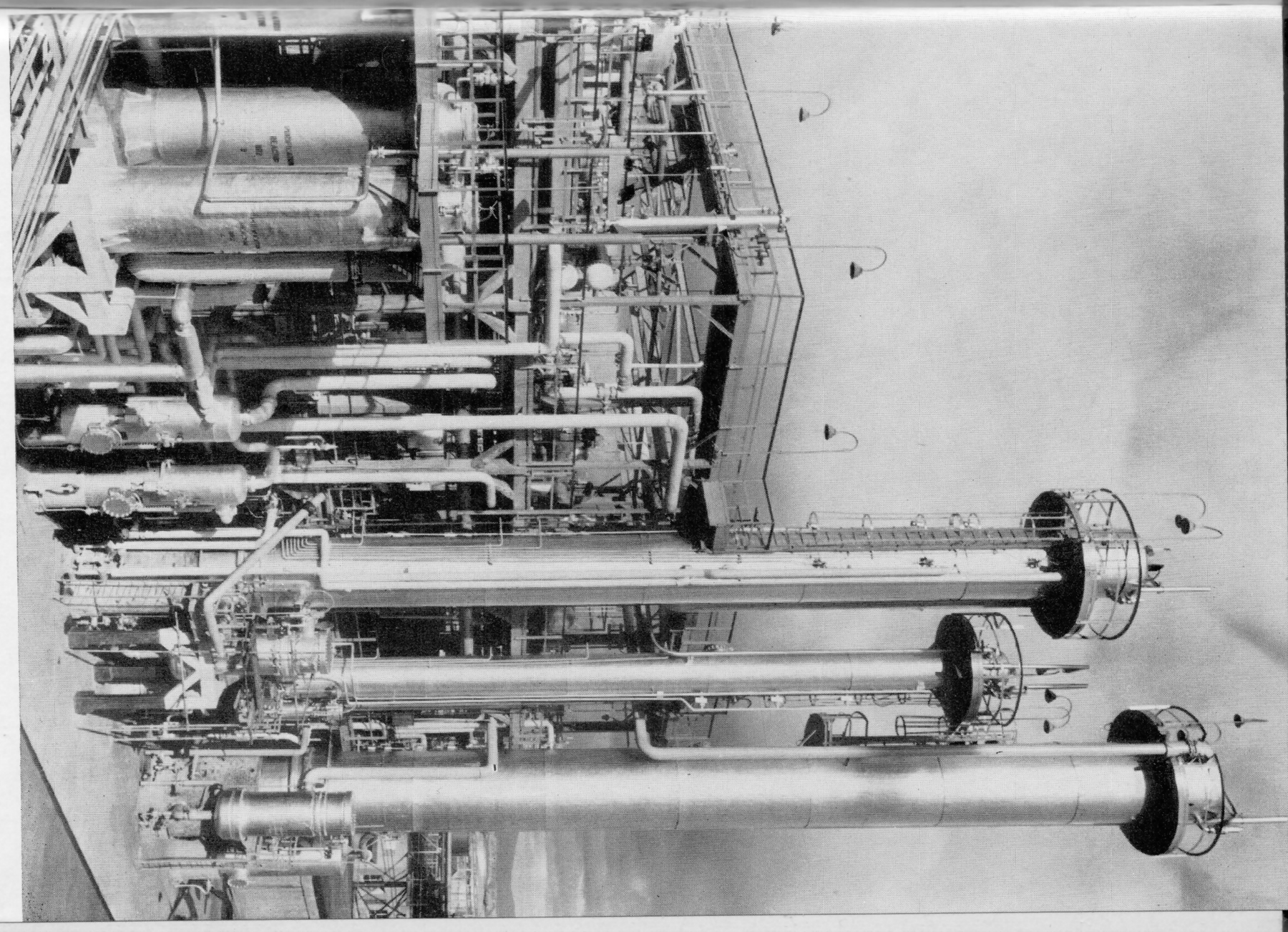
$$\underset{\text{acrolein}}{CH_2{=}CHCHO} + \underset{\substack{\text{isopropyl}\\\text{alcohol}}}{(CH_3)_2CHOH} \rightarrow \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} + \underset{\text{acetone}}{(CH_3)_2CO}$$

Allyl alcohol is treated with hydrogen peroxide in the presence of a



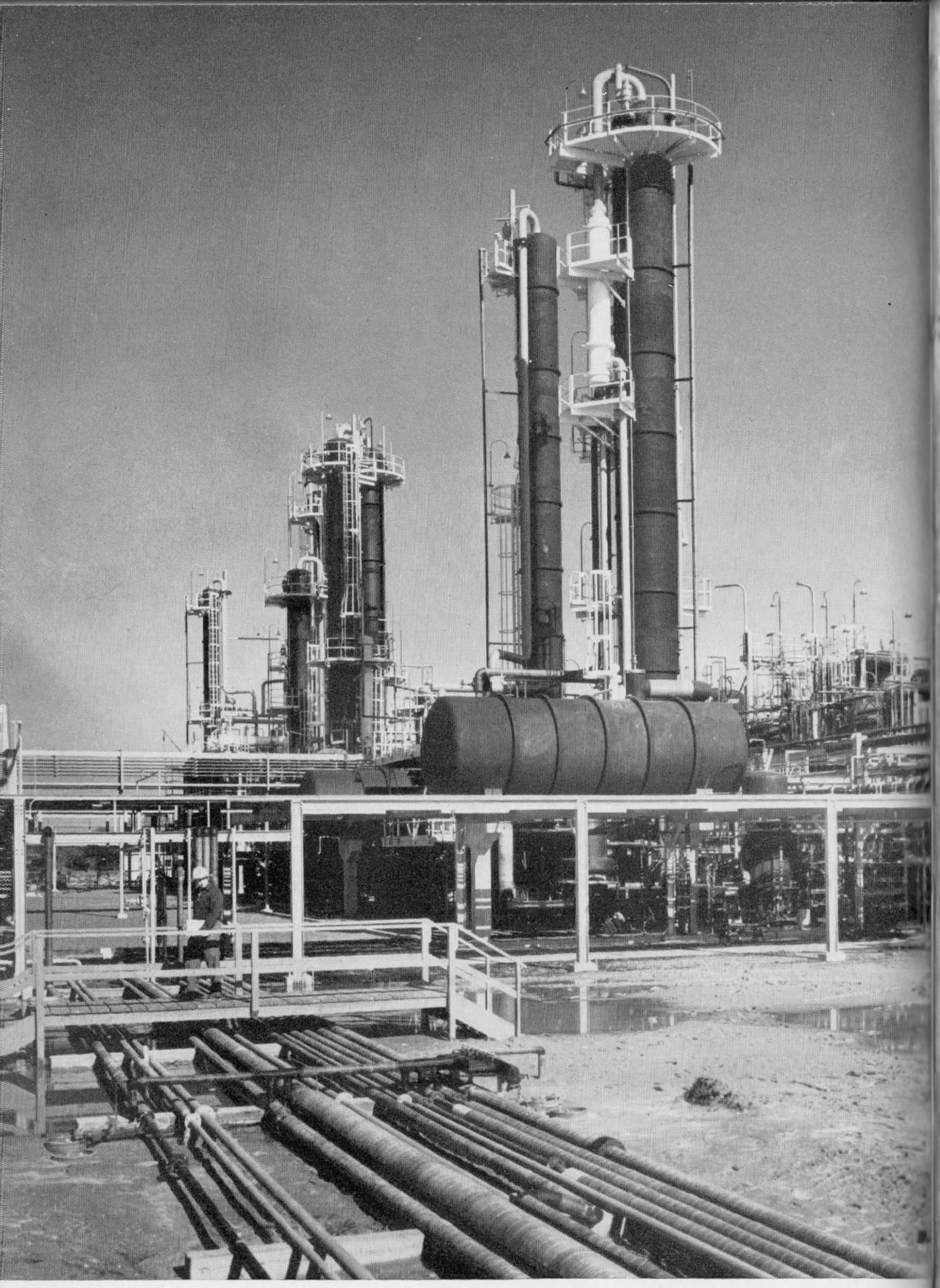
GLYCERINE FROM PROPYLENE (ACROLEIN ROUTE), AND HYDROGEN PEROXIDE FROM ISOPROPYL ALCOHOL

(Design by Shell Development Company – only major equipment illustrated)



Ethyl alcohol by direct hydration at Grangemouth, Scotland

Courtesy British Hydrocarbon Chemicals



The production of phenol from cumene at Gibbstown, New Jersey

Courtesy Hercules Powder Co.

tungstic oxide catalyst. By this means the double bond of the allyl alcohol is hydroxylated to give glycerine. This is a liquid phase reaction carried out at 60–70° C.

$$\underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} + \underset{\substack{\text{hydrogen}\\\text{peroxide}}}{H_2O_2} \rightarrow \underset{\text{glycerine}}{CH_2OHCHOHCH_2OH}$$

In the operation of this process on the basis of petroleum raw material, it may be anticipated that the hydrogen peroxide also will be a petroleum chemical, derived by the somewhat unexpected method of partial oxidation of isopropyl alcohol. This process is discussed later.

Variations can be effected on some of the steps. The complex, as described, has industrial ramifications extending well beyond the production of glycerine. Acrolein, allyl alcohol, hydrogen peroxide, isopropyl alcohol and acetone are all industrial products with substantial fields of interest outside the glycerine production requirements. The commercial evaluation of such a range of processes is clearly a complicated study.

Synthetic glycerine is still largely centred in the U.S.A., although there is now substantial capacity in Holland. Of the U.S. product, in 1960 approximately half, or about 140 million lb, was synthetic, all of it derived from petroleum.

With impending expansions, there will soon be capacity in the U.S.A. for a substantially greater production of synthetic glycerine, which will meet the developing requirements for some time to come.

The pattern of usage of glycerine in the U.S.A. in 1960 was as follows (in millions of lb):

	million lb
Alkyd resins	65
Cellophane	49
Drugs and cosmetics	46
Tobacco	39
Foods and beverages	22
Explosives	16
Miscellaneous and exports	41
	278

Hydrogen Peroxide

This should properly come under the heading of isopropyl alcohol derivatives. It has, however, no direct association with the other products considered under that heading, and it seems more appropriate to treat it separately. This is a development only just reaching commercial status, and competing on a normal basis with alternative processes based on inorganic or organic raw materials. The proportion of hydrogen peroxide which can currently be classed as petroleum-derived is extremely small.

Isopropyl alcohol is oxidized with pure oxygen in the liquid phase at 90–140° C and a pressure of 3–4 atmospheres. The reaction mixture is diluted with water and distilled to remove acetone and unreacted isopropyl alcohol. The hydrogen peroxide is recovered as a 6–10 per cent aqueous solution, contaminated with organic impurities. It is concentrated and purified by thermal or chemical methods.

$$\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} + O_2 \rightarrow \underset{\text{acetone}}{(CH_3)_2CO} + \underset{\text{hydrogen peroxide}}{H_2O_2}$$

Phenol

Here we have, once again, a situation in which a series of standard processes, based historically upon coal-derived benzene, has been supplemented by a petroleum chemical process. It is not necessary to dwell on the standard processes, which have been in operation for many years. In essence they are:

(*a*) Sulphonation of benzene, followed by caustic fusion.
(*b*) Chlorination of benzene, followed by hydrolysis with aqueous sodium carbonate.
(*c*) Chlorination, followed by high temperature vapour phase hydrolysis with steam.

The petroleum route proceeds by way of cumene (isopropyl benzene). Benzene may be alkylated with propylene either in the liquid or vapour phase. The liquid phase process, using sulphuric acid as catalyst, is now less common. In the vapour phase, benzene may be alkylated with propylene using a supported phosphoric acid catalyst at 250° C and 25 atmospheres. Aluminium chloride is an alternative catalyst.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{propylene}}{CH_2{=}CHCH_3} \rightarrow \underset{\text{cumene}}{C_6H_5CH(CH_3)_2}$$

Purified cumene is fed to an oxidation vessel, where it is emulsified with a dilute sodium carbonate solution. The emulsion is contacted with air and held at 130° C until 35–50 per cent of the cumene is converted to the hydroperoxide. Carrying the conversion too far involves an increased formation of by-products.

The crude reaction mixture is fed to an acidifier, containing a 10 per cent solution of sulphuric acid at 80–120° C, with the pressure atmospheric or slightly higher. Under these conditions, the cumene hydroperoxide is converted to phenol and acetone, with some acetophenone and methylstyrene as by-products.

$$\underset{\text{cumene}}{C_6H_5CH(CH_3)_2} + O_2 \rightarrow \underset{\substack{\text{cumene}\\\text{hydroperoxide}}}{C_6H_5C(CH_3)_2OOH}$$

$$\underset{\substack{\text{cumene}\\\text{hydroperoxide}}}{C_6H_5C(CH_3)_2OOH} \rightarrow \underset{\text{phenol}}{C_6H_5OH} + \underset{\text{acetone}}{(CH_3)_2CO}$$

The separation of the reaction products from each other and from unreacted cumene may be achieved by distillation or a mixture of distillation and extraction.

The cumene route to phenol has only been in commercial operation for a few years but it is already a significant factor in most of the major industrialized countries. Phenol is one of the most important industrial organic chemicals. Of the 1959 U.S. production of 309,000 long tons, 20 per cent was derived from cumene. In 1960 the total U.S. production rose to 345,000 long tons, compared with the United Kingdom production of 55,000 long tons (capacity for phenol from cumene in the United Kingdom is about 13,000 long tons annually). Production totals include natural phenol. Phenol consumption in the U.S.A. breaks down as follows:

Phenolic resins	53·6%
Miscellaneous chemicals	31·4%
Exports	5·0%
Miscellaneous	10·0%

Propylene Tetramer

Of the lower polymers of propylene, the tetramer is of major significance as a raw material for detergent production. The polymerization may conveniently be based on refinery C_3 streams containing

both propane and propylene. Supported phosphoric acid is the common catalyst, and the reaction conditions are typically 200–240° C and 15–25 atmospheres pressure.

Some production of the trimer also takes place, and this is largely used for the alkylation of phenols to produce alkyl phenols as raw materials for non-ionic detergents.

Benzene is alkylated with propylene tetramer at 5–60° C in the presence of a catalyst. Aluminium chloride and sulphuric acid have been used as catalysts, but hydrofluoric acid is now more common. The alkyl benzene is then purified by vacuum distillation.

The alkyl benzene (commonly referred to as dodecyl benzene) is an important commercial product. To obtain a finished detergent product, the alkyl benzene is first sulphonated and neutralized. The alkyl benzene sulphonate is then normally blended with 'builders' such as polyphosphates, silicates, etc., in a soap crutcher. The thick slurry is then spray dried to form the familiar 'beads' or small granules of packaged synthetic detergent.

Propylene Oxide

The production of propylene oxide forms a close analogy with the chlorohydrin route to ethylene oxide. Propylene chlorohydrin is produced from the reaction of hypochlorous acid and propylene. The conditions of operation are similar to those described for ethylene chlorohydrin manufacture. The reaction with propylene takes place more readily than with ethylene, but there is a greater tendency for by-product formation from chlorine addition reactions.

Aqueous alkali reacts with propylene chlorohydrin in a similar manner to ethylene chlorohydrin, but the reaction is more rapid.

There is, to date, no commercial development of a direct oxidation route to propylene oxide. In the vapour phase, the yields obtained by the use of a silver catalyst have proved too low for an economically feasible process. The patent literature makes it clear that the prospects of a liquid phase process are under active study.

The pattern of usage of propylene oxide and its derivatives offers some analogy to that of the ethylene homologues. Propylene glycol is a major derivative. Its esters with dibasic unsaturated acids form an important basis for the polyester resin industry. Propylene glycol also has significant usage in pharmaceuticals and cosmetics. A recent

development of outstanding promise is the production of polyethers (of which polypropylene glycols themselves offer an illustration of some commercial significance). These are typically high molecular weight adducts of a polyhydric alcohol (such as glycerine) with propylene oxide. The polyethers form an important component of the polyurethane resins.

The production of propylene oxide in the U.S.A. in 1959 was estimated as 130,000 long tons, and the propylene glycol production for the same year was put at 68,000 long tons.

Polypropylene

A great future is commonly predicted for polypropylene. The commercial development of this material has only been achieved within the past year or two. There is still a lot to be learned about production (and application) techniques.

It has already been pointed out that propylene is a highly desirable monomer for the production of plastics and rubbers, by virtue of its availability on an economic basis. In the case of polypropylene, this general observation has to be qualified by the fact that the usual propylene source (a C_3 stream containing 40–95 per cent of propylene) is normally purified to not less than 98 per cent propylene.

A Ziegler catalyst is employed in the manufacture of polypropylene to provide a regular molecular structure (referred to as an isotactic molecule). If there is a random arrangement of monomer units in the molecular chain, it is described as an atactic molecule. Commercial production of polypropylene has concentrated on the isotactic molecular form.

Polypropylene is more rigid and has a higher softening point than polyethylene. The only point at which polyethylene can so far offer an advantage as a construction material, is in impact strength at low temperatures.

It is too early to assess the full potential of polypropylene, since it is still at an experimental stage in many fields. Its resistance to boiling water offers important practical advantages over polyethylene in many spheres of domestic application, such as, for example, the whole range of domestic plumbing.

Some idea of its expected development can be deduced from

estimates of production. The capacity in the U.S.A. at the end of 1958 was 20 million pounds per year, and by the end of 1962 this is expected to rise to 545 million pounds per year. The estimate of sales for 1961 in the U.S.A. is 100 million pounds, rising to 260 million pounds in 1963.

For 1960 it has been estimated that the usage of polypropylene in the U.S.A. was as follows:

Injection moulding	50%
Fibres	30%
Film and sheet	6·5%
Miscellaneous	13·5%

Ethylene-Propylene Rubbers

These have already been considered under ethylene (page 75), but it is obvious that they also represent a significant potential usage of propylene.

Butyl Alcohols

n-Butyl and isobutyl alcohols may be produced from propylene by means of the Oxo reaction. This process originated in Germany, and is used industrially both in the U.S.A. and the United Kingdom. It is a means of extending the chain length of olefins and olefinic compounds.

The synthesis is a process whereby carbon monoxide and hydrogen are directly added to olefins to give aldehydes. It requires a cobalt catalyst, which in the active form becomes cobalt carbonyl.

Part of the industrial significance of the Oxo process is founded on the feasibility of this route as a means of producing primary alcohols from olefins. The more common petroleum chemical processes normally give secondary alcohols.

Propylene, dissolved in a high boiling solvent such as octane or butyl alcohol, is treated with an equimolar mixture of hydrogen and carbon monoxide in the presence of a cobalt compound (such as the naphthenate) soluble in the reaction mixture. The pressure is about 200 atmospheres and the temperature about 150° C. The reaction product is freed from catalyst and fractionated to give the aldehydes.

$$CH_3CH{=}CH_2 + CO + H_2 \rightarrow \underset{\text{n-butyraldehyde}}{CH_3CH_2CH_2CHO}$$

$$\rightarrow \underset{\text{isobutyraldehyde}}{CH_3CH(CH_3)CHO}$$

Where the reaction is to proceed to the production of alcohols, the cobalt-free reaction product is given a preliminary flash distillation to separate the high boiling components, and the aldehyde concentrate (containing some alcohol) is hydrogenated in a conventional manner using a cobalt or copper chromite catalyst at high pressure. The pure alcohols are separated by fractionation. The production of isobutyl and n-butyl alcohols was originally in the ratio 60 : 40, varying to some extent according to the pressure and catalyst used. Recent modifications of the process have been successful in effecting a substantial reduction in the proportion of isobutyl alcohol produced.

n-Butyl alcohol is also produced by fermentation, or from acetaldehyde via crotonaldehyde. Isobutyl alcohol is also a by-product of the synthesis of methyl alcohol.

As has already been pointed out, the main outlet for n-butyl alcohol is in the surface coatings field. Isobutyl alcohol has not yet found a wide industrial acceptance. It has similar properties to n-butyl alcohol, and the greater availability resulting from the development of the Oxo process is expected to assist in creating an increased demand.

Apart from its use in the synthesis of n-butyl alcohol, n-butyraldehyde has a number of other applications as a chemical intermediate.

The total production of butyl alcohols in the U.S.A. in 1960 was 278,000 long tons. In recent years this has generally been subdivided into almost one half secondary butyl alcohol, slightly less than one half n-butyl alcohol, and the small balance isobutyl alcohol.

Acrylonitrile and Acrolein

Acrylonitrile is produced on a substantial scale both from acetylene and from ethylene. Acrolein is already being produced from propylene as part of the most recent glycerine production complex. A new process has recently been announced which makes interesting claims relating to the manufacture of acrylonitrile or acrolein from

propylene. This process commonly involves the use of bismuth phosphomolybdate as catalyst.

Propylene, ammonia and air are reacted, in the presence of the solid catalyst, in the vapour phase. The preferred temperature range is 425–510° C and the reaction pressure is approximately atmospheric.

$$\underset{\text{propylene}}{CH_3CH{=}CH_2} + NH_3 + 1\tfrac{1}{2}O_2 \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN} + 3H_2O$$

Acrylonitrile is the main product, and the by-products, apart from oxides of carbon, are acetonitrile and acrolein. An increase in the ratio of ammonia to propylene will suppress acrolein formation. The yields obtained by this process are not high, but this is offset by the relatively simple nature of the process, and the low cost of the starting materials. It will be noted that this process eliminates the use of hydrogen cyanide as a raw material. This is a highly desirable feature since hydrogen cyanide is a difficult material to handle, in addition to being very highly poisonous.

In adapting the process to produce acrolein, it is possible, though not necessary, to modify the catalyst. Propylene will react with oxygen in the presence of water at 425–450° C to give acrolein. By-products are mainly acetaldehyde, acetic acid and acrylic acid. In this case the yield of acrolein at about 70 per cent is higher than that for acrylonitrile in the alternative process.

A further modification of the acrylonitrile process is independently undergoing commercial development. In this case propylene is treated with nitric oxide instead of ammonia and oxygen. This may be regarded as a two-step operation based on propylene, ammonia and oxygen as the original starting materials. In this case, however, the reaction is required to be carried out at 700° C in the presence of a supported silver catalyst.

These new acrylonitrile processes again illustrate the trend towards simplified processes and economical raw materials even at the cost of reduced yields.

Acetone by the Wacker Process

Reference has already been made to the production of acetone from propylene via isopropyl alcohol, and also to the incidental production of acetone in a variety of other processes. A further interesting prospect is represented by the use of the Wacker process to develop a direct synthesis of acetone from propylene.

The original basis of the Wacker process, as has already been described, was for the oxidation of ethylene to acetaldehyde, using palladium chloride promoted by cuprous chloride. The same principle can be applied to the oxidation of propylene, in which case acetone is the major product.

The process, in this form, is still in the experimental stage, but it offers considerable promise as an economic route to acetone, where additional production of isopropyl alcohol is not required. The commercial development of the process may be hindered by the availability of so many new processes with capacity for by-product acetone. In the long term, however, the Wacker process for acetone production is likely to prove a significant factor.

Isoprene

Isoprene has for a number of years been a product of some interest as a minor copolymer with isobutylene in butyl rubber production. As it was required to the extent of only about 2–3 per cent of the monomer mixture, the tonnage involved was relatively slight. Interest in isoprene has been stimulated by the recent development of polyisoprene rubber on the commercial scale. The existing production is based on the dehydrogenation of C_5 olefins (present in cracked gasoline fractions), in plant already constructed for the dehydrogenation of butylenes to butadiene. Where it is necessary to consider developing production of isoprene in the absence of any existing facilities, it has been suggested that the most economical approach is likely to be based on the initial preparation of a propylene dimer (the required isomer is 2-methylpentene-2). Pyrolysis of the propylene dimer results in the elimination of a methane molecule, and the production of isoprene. This process is still at the design stage.

The particular significance of polyisoprene is that it is chemically almost identical with natural rubber. It therefore differs in its applications from most earlier forms of synthetic rubber, as discussed in Chapter 16.

Chapter 9

Derivatives of C_4 Hydrocarbons

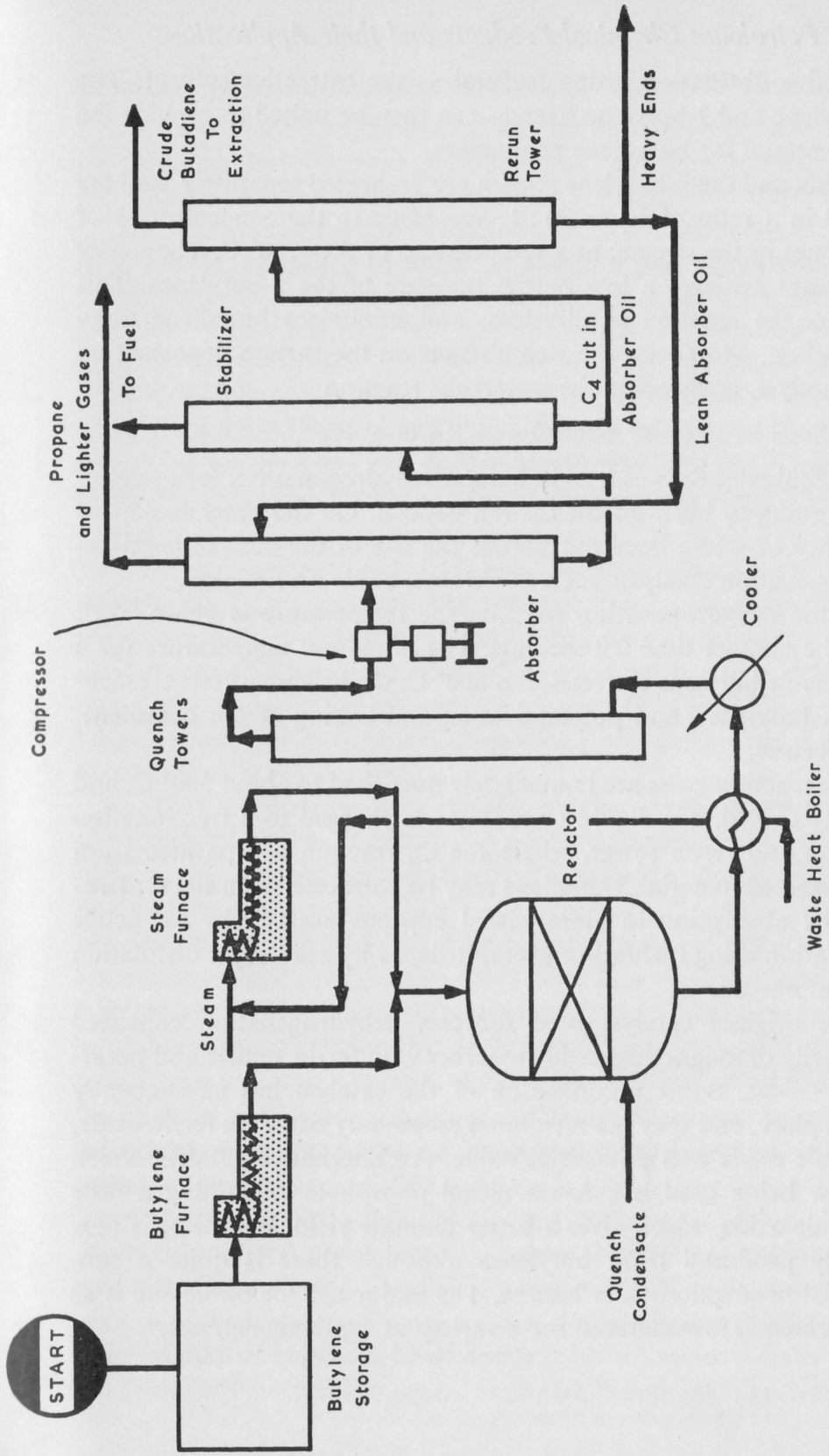
The derivatives of butane, notably from its dehydrogenation and its oxidation, have already been considered under the heading of higher paraffins. The raw materials which are to be considered under this heading are the n-butylenes, isobutylene and butadiene.

Consumption of butylenes in the U.S.A. in 1960 may be summarized as follows:

Product	*Butylene Consumption (thousand tons)*	*% Butylene Consumption*
Butadiene	1,218	78·5
Secondary butyl alcohol	109	7·0
Butyl rubber	94	6·1 (isobutylene)
Polybutylene	42	2·7
Oxo alcohols	19	1·2
Alkyl aromatics	10	0·6
Tertiary butyl alcohol	12	0·8 (isobutylene)
Diisobutylene	19	1·2 (isobutylene)
Polyisobutylene	12	0·8 (isobutylene)
Others	17	1·1
	1,552	100·0

Butadiene from Butylenes

The C_4 gas fraction obtained in the refinery requires some form of treatment to isolate the n-butylenes. A variety of techniques can be applied. Initially, straight fractional distillation can be used to separate isobutylene, isobutane and 1-butylene, on the one hand, from n-butane, cis- and trans-2-butylene on the other. The first of these fractions may be passed through 65 per cent sulphuric acid to remove isobutylene. It is then possible to separate and recover the isobutylene either as the dimer or as tertiary butyl alcohol. Isobutane and n-butane can be separated from their respective fractions by



BUTADIENE FROM BUTYLENES
(Design by Esso Research and Engineering Company)

extractive distillation, using furfural as the extractive solvent. The 1-butylene and 2-butylene streams can then be united to provide the raw material for butadiene production.

Steam and the n-butylene stream are preheated separately, and are mixed in a ratio of 15 or 20 : 1, according to the concentration of butylenes in the stream, at a temperature of 600–700° C. The use of the steam achieves a low partial pressure of the n-butylenes. This favours the reaction equilibrium, and minimizes butadiene polymerization. Moreover, the steam reacts on the carbon deposited on the catalyst, undergoing the water–gas reaction

$$C + H_2O \rightarrow CO + H_2$$

This eliminates the need, as in butane dehydrogenation, for cycles of air burning to burn off the carbon deposit. On the other hand, the presence of steam does not permit the use of the conventional dehydrogenation catalysts such as chromic oxide on alumina.

In the dehydrogenation reactors the temperature is 625–675° C, and the contact time 0·2 seconds. The minimum temperature for a reasonable butylene conversion is 600° C, whilst above 700° C cracking of butylenes, and polymerization and coking of the butadiene, will occur.

The reaction gases are immediately quenched to about 500° C, and further cooled. The liquid condensate is charged to a fractionation column and rerun tower, where the C_4 fraction is separated from polymerized material. Butadiene may be extracted from the C_4 fraction by absorption in ammoniacal cuprous acetate, by extractive distillation using furfural or acetonitrile, or by azeotropic distillation with ammonia.

The original catalyst used for this dehydrogenation consisted primarily of magnesium oxide together with ferric, cupric and potassium oxides. Some modification of the catalyst has subsequently taken place, and they are now more commonly based on ferric oxide, chromic oxide and potassium oxide. An alternative catalyst which is now being used is calcium nickel phosphate containing a little chromic oxide, which gives a better ultimate yield. Butadiene is now mostly produced from butylenes although there is quite a substantial production from butane. The major use for butadiene is as the principal raw material for a variety of synthetic rubbers.

Secondary Butyl Alcohol and Derivatives

The hydration of butylenes to secondary butyl alcohol bears a considerable similarity to the production of isopropyl alcohol from propylene by the concentration–dilution process.

The raw material for this operation is commonly a refinery C_4 gas stream. It is necessary to remove butadiene and isobutylene. The small proportions of butadiene which may commonly be present are selectively hydrogenated to butylene using a nickel sulphide or copper catalyst. The extraction of larger proportions of butadiene may require more elaborate separation techniques, such as absorption, extractive distillation, etc. Isobutylene may conveniently be eliminated by absorption in 65 per cent sulphuric acid. The gas stream is passed through the acid at 10–20° C. The 'fat' acid, containing absorbed isobutylene, may subsequently be heated to 80–100° C for about 30 minutes. Polymers of isobutylene will then separate out as an upper layer. Eighty per cent of the polymer fraction is in the form of the dimer. Diisobutylene, separated in this way, can be used as the alkyl fraction in the production of an alkyl phenol as a detergent ingredient. It may also be used as raw material for Oxo synthesis, whereby nonanol is obtained. Nonanol is an alcohol used in the manufacture of plasticizers.

The C_4 hydrocarbons fed to the acid reaction comprise the butanes and n-butylenes. The butanes pass unchanged through the process, and, as a residual gas fraction, may be returned for refinery use. The liquid phase acid reaction may be carried out using 75–85 per cent sulphuric acid at about 20–35° C. Particular care must be taken with the reaction conditions in this case since there is a marked tendency to form polymer by-products. The main product of the acid reaction is butyl hydrogen sulphate. This is diluted with water and heated to hydrolyse it to secondary butyl alcohol. The alcohol is stripped from the dilute acid solution with steam. Sulphuric acid is recovered from the bottom of the strippers, in a relatively dilute form, and concentrated for re-use.

$$\underset{\text{1-butylene}}{CH_3CH_2CH{=}CH_2} + H_2SO_4 \rightarrow \underset{\text{butyl hydrogen sulphate}}{CH_3CH_2CH(OSO_3H)CH_3}$$

$$\underset{\text{2-butylene}}{CH_3CH{=}CHCH_3} + H_2SO_4 \rightarrow \underset{\text{butyl hydrogen sulphate}}{CH_3CH_2CH(OSO_3H)CH_3}$$

$$\underset{\text{butyl hydrogen sulphate}}{CH_3CH_2CH(OSO_3H)CH_3} + H_2O \rightarrow \underset{\text{secondary butyl alcohol}}{CH_3CH_2CHOHCH_3} + H_2SO_4$$

Both 1-butylene and 2-butylene give the same alcohol on hydration. Crude secondary butyl alcohol is taken overhead from the steam stripper, and is concentrated and purified by distillation.

Direct hydration processes have not been successfully applied to butylenes on account of the excessive formation of polymer.

Secondary butyl alcohol has some limited uses as a solvent and as a chemical intermediate, but the great bulk of it is converted to methyl ethyl ketone. The process is similar in principle to the conversion of isopropyl alcohol to acetone. The dehydrogenation reaction takes place in the vapour phase over a catalyst bed of zinc oxide or brass at atmospheric pressure and 350–550° C. The reaction products are cooled, and the condensed liquids fractionated to separate methyl ethyl ketone. The hydrogen stream is scrubbed to remove any entrained alcohol or ketone, and may then be used for hydrogenation processes elsewhere. It is also possible to produce methyl ethyl ketone from secondary butyl alcohol by a process of catalytic oxidation, but this is not very common in practice.

$$\underset{\text{secondary butyl alcohol}}{CH_3CH_2CHOHCH_3} \rightarrow \underset{\text{methyl ethyl ketone}}{CH_3CH_2COCH_3} + H_2$$

Nearly all methyl ethyl ketone is derived from secondary butyl alcohol, but a small amount is also made from the oxidation of paraffins.

Methyl ethyl ketone is a low-boiling solvent used primarily in the lacquer industry, where it has offered competition in the field traditionally held by ethyl acetate.

It also has an important application on a smaller scale in the solvent dewaxing of lubricating oil fractions. Production of methyl ethyl ketone in the U.S.A. amounted in 1960 to about 105,000 long tons.

Polybutenes (polybutylenes)

The term polybutenes commonly refers to products in the molecular weight range 300–1,900. Refinery C_4 gas streams (containing a mixture of butylenes together with some isoparaffins) are polymerized in the presence of aluminium chloride, with hydrochloric acid as activator. The temperature of the polymerization is the major factor controlling the viscosity and molecular weight of the finished product. The polymerization is exothermic, and heat is removed from the reactor by a refrigerated tube bundle.

Somewhere around 90 million lb of polybutenes were consumed in the U.S.A. in 1960. Major uses are in lubricating oils, caulking compounds, and sealers.

The normal term for these compounds is polybutenes, distinguishing them from the higher molecular weight polyisobutylenes discussed under the next heading. These products do contain a fraction of polyisobutylene and the position is occasionally confused by the use of this term to describe them.

Isobutylene Derivatives

Under the previous heading, reference was made to the incidental production of diisobutylene in the course of removing isobutylene from a C_4 gas stream by sulphuric acid absorption.

Using a low acid strength and low temperatures, it is alternatively possible to hydrate isobutylene by sulphuric acid to tertiary butyl alcohol. The usual range of conditions is 50–65 per cent sulphuric acid concentration, and a temperature of 10–30° C.

$$\underset{\text{isobutylene}}{(CH_3)_2C{=}CH_2} + H_2O \rightarrow \underset{\substack{\text{tertiary butyl}\\\text{alcohol}}}{(CH_3)_2COHCH_3}$$

The tertiary butyl alcohol is separated from the acid liquor by dilution with water or by solvent extraction. It is of no great importance as a solvent, but is used as a raw material in the production of tertiary butyl phenol, which is an intermediate for oil-soluble phenol-formaldehyde resins.

Commercial polyisobutylenes, with molecular weights ranging from 3,000 to 200,000, can be prepared by a variety of techniques. Polymerization is usually carried out at low temperatures (below 0° C) with the aid of Friedel–Crafts catalysts, such as aluminium chloride or boron trifluoride.

The products range from sticky fluids to elastic semi-solids. They are used for coatings and plasticizers, frequently mixed with paraffin wax or polyethylene.

Isobutylene is a versatile and reactive chemical intermediate, whose full potentialities have probably not yet been developed. At the present time its most important outlet is in the production of butyl rubber.

Butyl rubber is a co-polymer of isobutylene with about 2–3 per

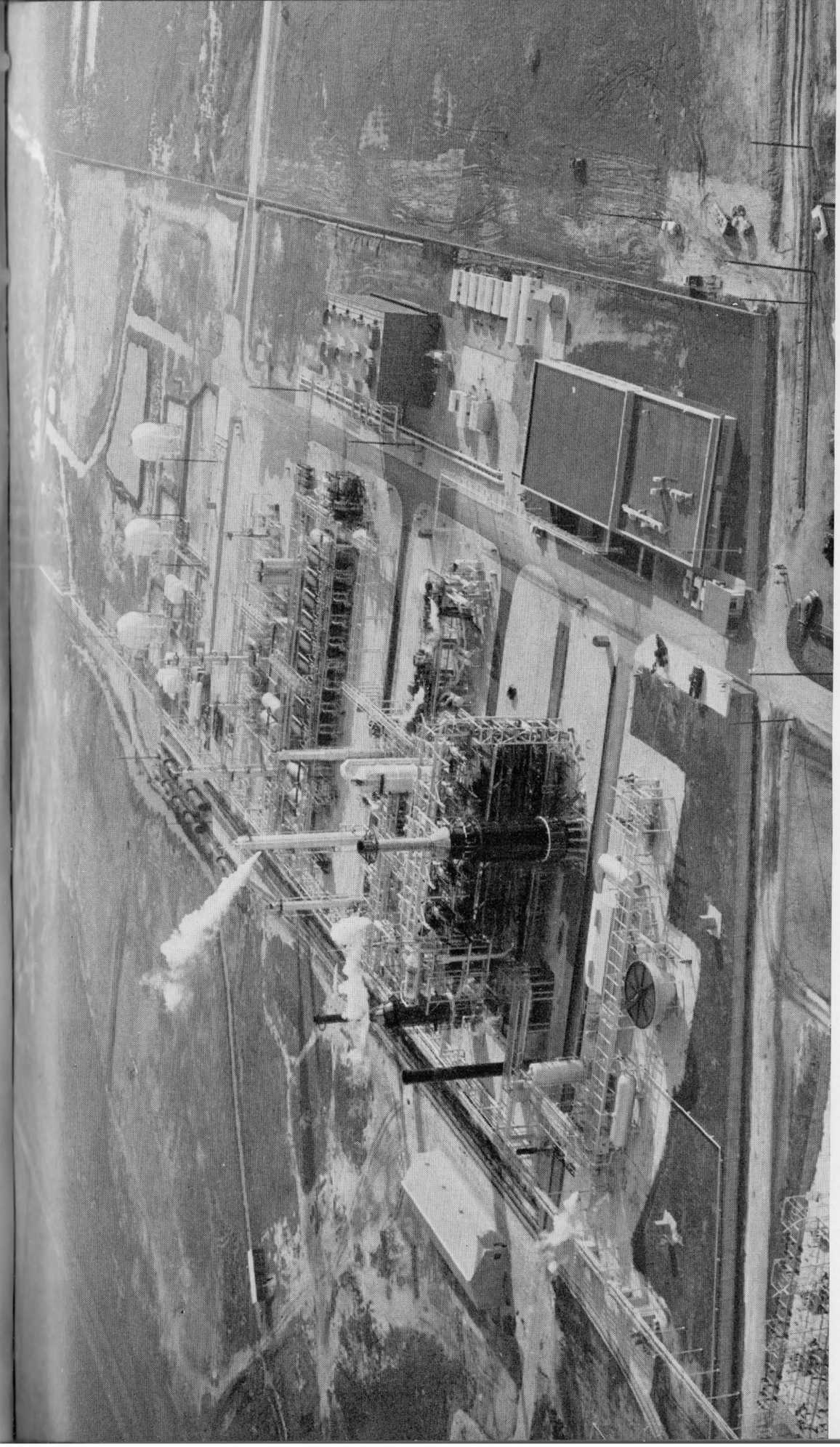
cent of isoprene. The co-polymerization is carried out at very low temperature (the feed temperature will usually range between minus 90 and minus 100° C). The solution of a Friedel–Crafts catalyst, such as aluminium chloride or boron trifluoride, is also injected into the reactors. A large amount of heat is evolved in the polymerization reaction, and this is removed by circulating liquid ethylene through cooling coils (keeping the temperature at about minus 95° C). A slurry of small rubber particles is formed, and the solvents and unreacted hydrocarbons are flashed off, using hot water. Antioxidants and zinc stearate are added, and after vacuum stripping the rubber crumb is dried, milled and packaged.

The main application for butyl rubber has been for tyre inner tubes, for which purpose its low permeability to air makes it particularly suitable. It also has good resistance to a wide range of solvents and chemicals, and has good electrical properties. These characteristics are assuming some importance today, since the original market for inner tubes is suffering from the arrival of the tubeless tyre. In certain respects butyl rubber would appear to offer considerable advantage for the production of tyres, but some of its characteristics, such as a lack of 'tack' (or bonding power), make it unsuitable for tyre production by currently conventional processes. Such difficulties can be overcome, but the cost factor then becomes a problem.

Butadiene Derivatives

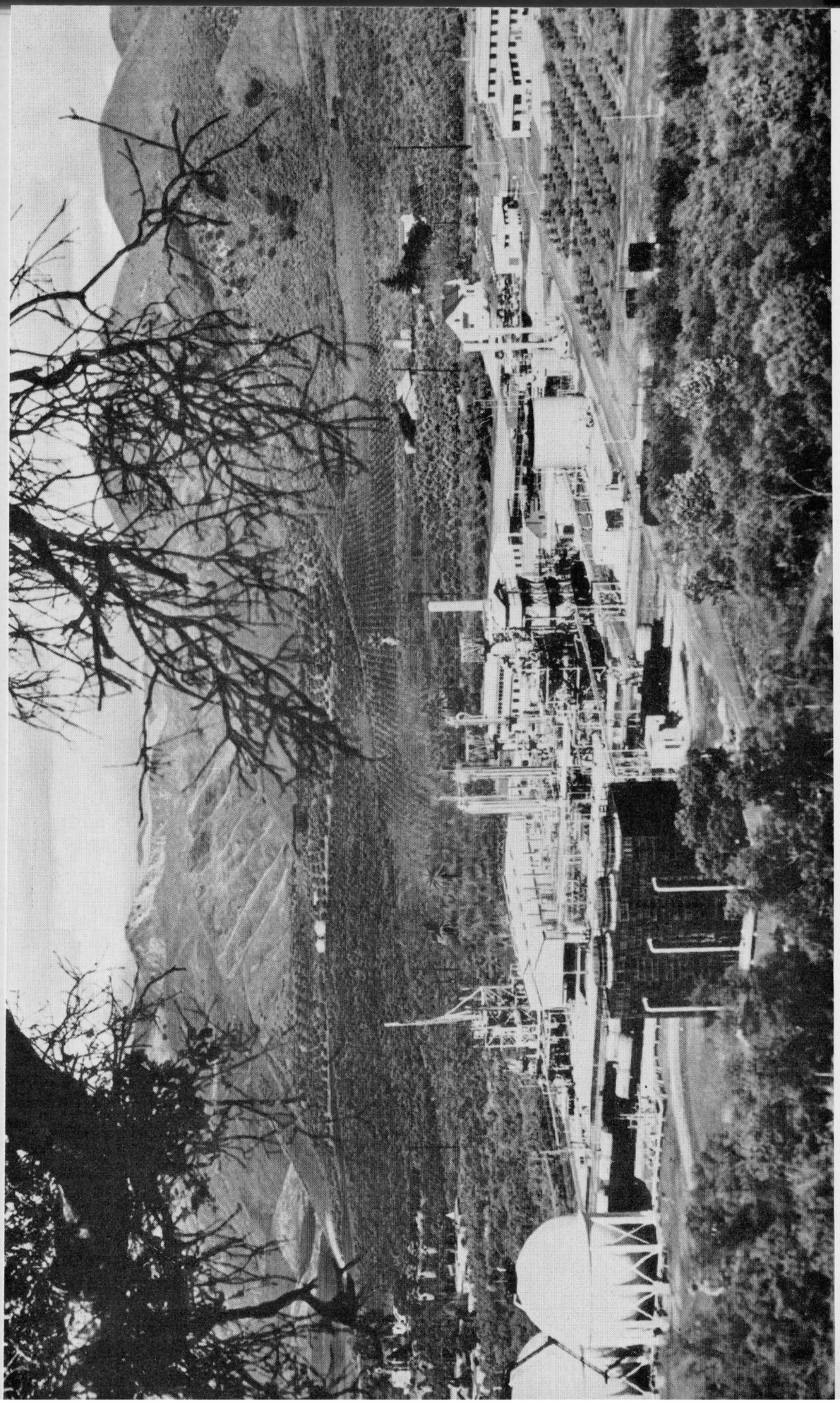
Butadiene was produced on a very considerable scale during the second world war in the course of the U.S.A. emergency rubber programme. There was a temporary lull in butadiene requirements after 1945, and this period saw the initiation of many investigations into the possibilities of butadiene as a chemical intermediate.

A process which has become of some commercial importance originates in the chlorination of butadiene to give 1,4-dichloro-2-butylene. The reaction produces a mixture of the 1,4- and 1,2-isomers, but the latter is separated and recycled to the reaction to suppress the formation of additional quantities. This is treated with sodium cyanide in the presence of cuprous salts. The 1,4-dicyano-butylene produced is successively hydrogenated to adiponitrile and hexamethylenediamine.



The production of butadiene from butylene at Orange, Texas

Courtesy Firestone Tire and Rubber Company



The ammonia plant at Ventura, California, is pleasantly situated among citrus orchards

Courtesy Shell Chemical Co., U.S.A.

$$\underset{\text{1,4-dichloro-2-butylene}}{CH_2ClCH{=}CHCH_2Cl} \xrightarrow{2NaCN} \underset{\text{1,4-dicyanobutylene}}{CNCH_2CH{=}CHCH_2CN}$$

$$\underset{\text{1,4-dicyanobutylene}}{CNCH_2CH{=}CHCH_2CN} + H_2 \rightarrow \underset{\text{adiponitrile}}{CNCH_2CH_2CH_2CH_2CN}$$

$$\underset{\text{adiponitrile}}{CNCH_2CH_2CH_2CH_2CN} + 4H_2 \rightarrow \underset{\text{hexamethylenediamine}}{NH_2(CH_2)_6NH_2}$$

Hexamethylenediamine is a major raw material in the production of nylon 66, the most common form of nylon salt.

Another process which is operated on a limited commercial scale is the treatment of butadiene with sulphur dioxide, under conditions of raised temperature and pressure. This reaction forms a sulphone which, on hydrogenation, yields tetramethylene sulphone, known commercially as 'Sulfolane'.

$$\underset{\text{butadiene}}{CH_2{=}CHCH{=}CH_2} + SO_2 \rightarrow \underset{\text{Sulfolane}}{\overset{CH_2-CH_2}{\underset{CH_2\quad CH_2}{\diagdown\ \diagup}}\!SO_2} \quad (+H_2)$$

Sulfolane is a product with considerable promise as a selective solvent for extractive distillation and solvent extraction processes. It has a very high selectivity as a solvent for aromatics.

There are many other interesting chemical possibilities for the use of butadiene, but there has been an ever-increasing demand from the synthetic rubber industry, which now consumes appreciably over 90 per cent of the butadiene produced (amounting in 1960 to 840,000 long tons in the U.S.A. alone).

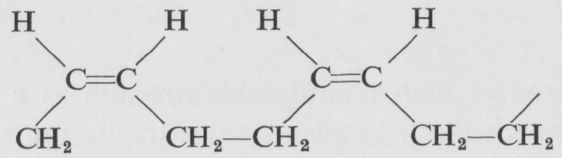
SBR is the designation of the most common form of synthetic rubber, derived from the co-polymerization of butadiene and styrene in the approximate proportion of 3 to 1 by weight. The polymerization may be effected as an emulsion process in water. Amongst the additional components, a catalyst is added to promote the polymerization and a stabilizer to keep the rubber particles in suspension. Some heat is applied to start the reaction, but subsequent cooling is necessary since the reaction is exothermic. It is required to maintain a fairly low temperature in the polymerization vessel, since the 'cold rubber' produced under these conditions has the best physical properties. The latex obtained is stripped of unreacted material, and coagulated to 'crumbs' which are dried and baled.

SBR is now the major component of tyres for ordinary passenger cars, although it is not suitable for the larger and heavier truck or aeroplane tyres, owing to its liability to overheating when so used.

By increasing the proportion of styrene in the co-polymer, speciality rubbers may be developed for compounding to impart higher resistance to abrasion. Other co-polymers of butadiene and styrene form the basis of certain paints and resins.

NBR represents the nitrile rubbers which are produced by the co-polymerization of butadiene and acrylonitrile. These are specialized rubbers, owing their significance to an exceptional degree of resistance to hydrocarbon solvents, more particularly the aromatics.

Butadiene may be directly polymerized at fairly low temperatures (5–35° C) by processes such as emulsion polymerization, under the influence of soaps, activators and modifiers. The properties of the finished polymers are very dependent upon the molecular configuration. Where the polymer takes the cis-1,4-structure, its properties become closely akin to those of natural rubber.



The development of the Ziegler catalysts has made it possible to produce such stereo-specific polymers. The polymerization is carried out in the liquid phase at moderate temperatures and pressures. A very substantial commercial development of this process is impending. It is proposed to use polybutadiene in conjunction with natural rubber rather than as a complete replacement.

Chapter 10

Derivatives of Higher Olefins

Reference has already been made to the possibility of producing isoprene from propylene. The specific interest of isoprene arises from the development of polyisoprene rubbers, which are competitive, not with other synthetic rubbers such as SBR, but with natural rubber. The economic requirement is that the isoprene monomer must be produced at a purity of no less than 97 per cent on a basis which will permit the polymer to compete effectively with natural rubber.

The commercial production of isoprene for polyisoprene, so far carried out, involves the joint use of facilities originally built for the dehydrogenation of butylenes to butadiene. C_5 unsaturates in cracked gasoline may be similarly dehydrogenated to isoprene. Further expansion of capacity for polyisoprene is under construction.

There has already been reference to the use of diisobutylene as a raw material for Oxo synthesis. In a similar way, other long-chain olefins may be converted to the corresponding primary alcohol with one extra carbon atom. Olefins in the C_5–C_8 range, either separately or as distillation fractions, may be converted to the C_6–C_9 primary alcohols. The main market for such alcohols is in the production of their esters as plasticizers. Olefins with a chain length in the C_9–C_{18} range may also be subjected to Oxo synthesis to produce primary alcohols in the range C_{10}–C_{19}. These primary alcohols may then serve as raw material for primary alkyl sulphate detergents. In practice these primary alcohols have more commonly been produced by the reduction of fatty acids.

Probably the most significant commercial application of long-chain olefins is the process of sulphation to produce secondary alkyl sulphates. Olefins of an appropriate fraction (which may be approximately C_{12}–C_{18}) may be obtained from wax cracking or from purified fractions of shale oil distillates. The sulphation is effected at 10–20° C with sulphuric acid of at least 90 per cent concentration. The contact

time is short. The main reaction is monosulphation, but some undesired dialkyl sulphate is formed.

$$RCH{=}CH_2 + H_2SO_4 \rightarrow \underset{\displaystyle OSO_3H}{\overset{\displaystyle RCHCH_2}{|}} \quad \text{alkyl sulphate}$$

$$2RCH{=}CH_2 + H_2SO_4 \rightarrow (RCH_3CH)_2SO_4 \quad \text{dialkyl sulphate}$$

Dilution of the reaction products with water allows olefin polymers to separate. The acid layer is neutralized. Aqueous isopropyl alcohol is added, and the solution extracted with a light hydrocarbon to remove any remaining olefin or dialkyl sulphate. Any dialkyl sulphate in the extract is hydrolysed with aqueous sodium hydroxide at 80° C to monoalkyl sulphate, and this is combined with the main production.

Secondary alkyl sulphate detergents are more commonly used in the liquid form, and in recent years have formed a component in detergent blends developed to provide a balance of desirable properties.

Controlled polymerization of ethylene using Ziegler catalysts will provide alpha olefins. This could represent a means of synthesis of primary alcohols by way of the Oxo reaction. The manufacture of such alcohols is being commercially developed on the basis of producing the appropriate aluminium alkyls in stoichiometric quantities for subsequent oxidation and hydrolysis to form primary alcohols.

B. PRODUCTS FROM MISCELLANEOUS PETROLEUM SOURCES

Chapter 11

Derivatives of Synthesis Gas

Synthesis gas is the common designation for a mixture of hydrogen and carbon monoxide which may form the basis for the synthesis of ammonia or methyl alcohol, and for the Fischer–Tropsch reaction. The application of synthesis gas to the Oxo reaction, for the production of aldehydes and primary alcohols from olefins, has already been described.

The production of synthesis gas did not start with petroleum chemicals. The search for a process for the fixation of nitrogen, which culminated in the production and application of synthesis gas in the manufacture of synthetic ammonia, is commonly regarded as one of the most stirring episodes in the development of the chemical industry prior to 1914. The original production was based on coke.

Ammonia and its Derivatives

It is not proposed to attempt any full account of ammonia production, but to give some indication of the influence of petroleum raw materials on an already flourishing large-scale industry.

The basic coke water–gas reaction is as follows:

$$C + H_2O \rightarrow CO + H_2$$

Each molecule of carbon monoxide is replaced by a molecule of hydrogen using the shift reaction. (It should perhaps be mentioned that in earlier terminology this has sometimes been called the water–gas equilibrium.)

$$CO + H_2O \leftrightharpoons CO_2 + H_2$$

It is also required to purify the hydrogen and to introduce nitrogen into the mixed gas stream. Using coke as a raw material the nitrogen is commonly introduced at an early stage, during the blow run of the water–gas generators (i.e. that portion of the cycle which builds up the temperature in the fuel bed). The mixture of nitrogen and hydrogen, appropriately purified, is reacted at high pressure in contact with a catalyst to complete the deceptively simple equation,

$$N_2 + 3H_2 \leftrightharpoons 2NH_3$$

This, in principle, was the basis of ammonia production from coke before the advent of petroleum chemicals. The first production of ammonia from natural gas dates back to 1930.

The original process used to recover hydrogen from natural gas was a thermal cracking process, and this is still in operation:

$$CH_4 \rightarrow C + 2H_2$$

The hydrogen stream from such an operation is more concentrated than with most other processes and the purification techniques may therefore be less elaborate. The most successful basis of purification is low temperature separation. The carbon black also obtained from this cracking process (a type known as a 'thermal' black) has certain uses in rubber and surface coatings. The application of this particular process has not developed widely, since it is less economical in the use of natural gas than alternative processes subsequently developed.

The next development in the use of natural gas dates back to the early 1930's with the advent of the methane–steam reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

A comparison of this reaction with the coke water–gas reaction will illustrate clearly that this is a more favourable basis for the production of hydrogen.

A similar type of reaction can be drawn up for any hydrocarbon, and techniques have in fact been devised to apply such a reaction to a wide range of products from methane up to fractions in the gasoline range. The hydrogen present in the hydrocarbon assists in the production of a synthesis gas containing appreciably more hydrogen than carbon monoxide. Whilst the shift reaction will subsequently provide a molecule of hydrogen for each molecule of carbon monoxide reacted, it is economically favourable to start with the maximum

hydrogen content in the crude synthesis gas. This ensures that the production of carbon dioxide in the shift reaction is minimized, and corresponding savings are made in the cost of its ultimate removal.

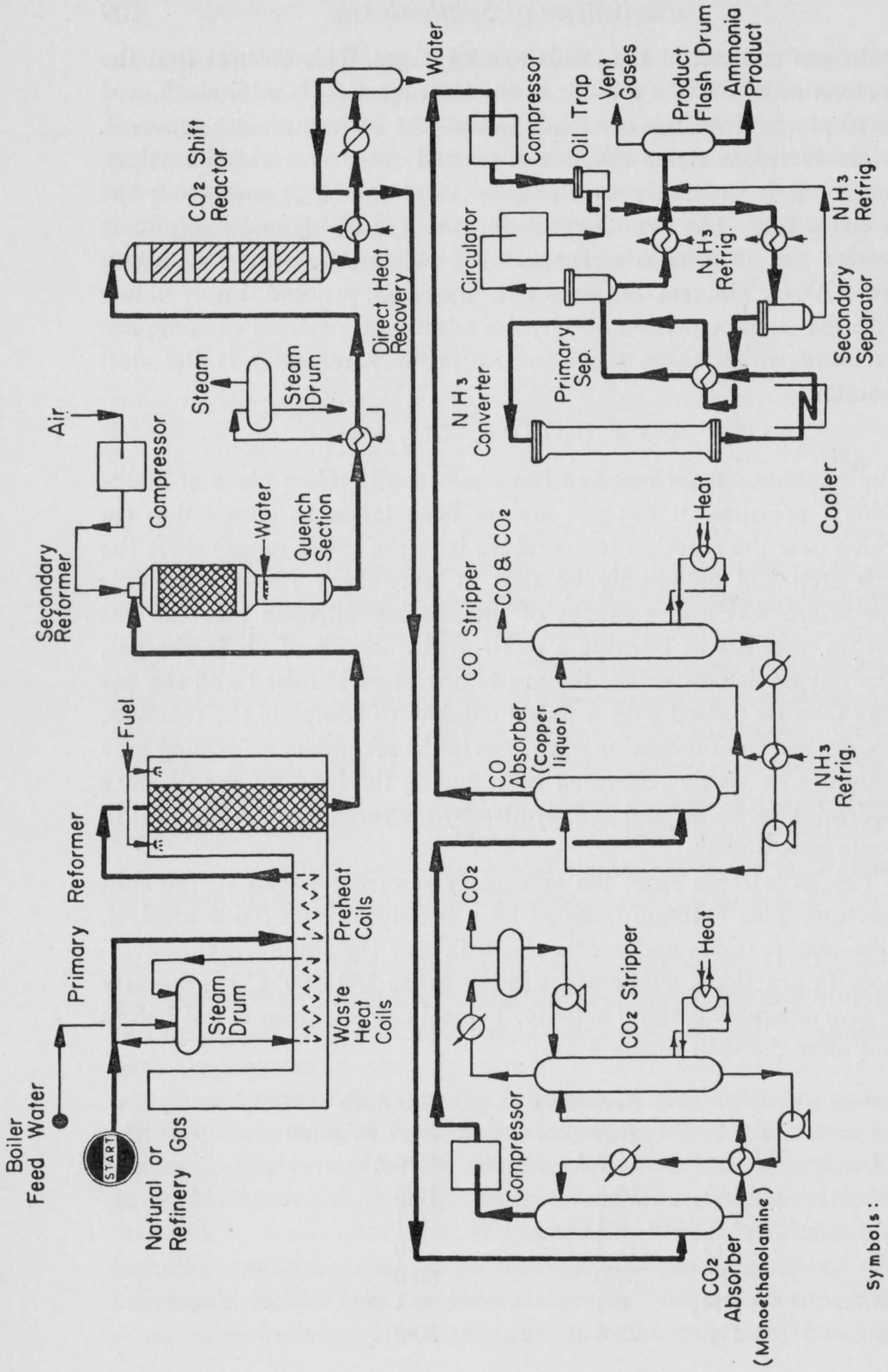
The methane–steam reaction is carried out over a nickel catalyst, so that it is necessary to eliminate sulphur compounds from the methane feed. The overall reaction, which is highly endothermic, is carried out in a tubular furnace (or primary reformer) at about 700–870° C. The reaction does not, of course, proceed simply in line with the single equation above. An additional reaction of some importance which takes place in the primary reformer is the shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The methane–steam reaction has traditionally taken place at atmospheric pressure. It has not always been taken to completion (in which case the reaction temperature is in the lower range) since the next step will commonly be that of 'secondary reforming'. This operation, which is a means of introducing nitrogen into the gas stream, consists of burning a controlled quantity of air in the gas. The oxygen is consumed, the gas temperature is raised and the gas may then be passed over a nickel catalyst to complete the reaction. Energy lost by combustion of the gas in the secondary reforming may therefore be partly recovered by reducing the load on the primary reforming furnaces, and usually also by the recovery of waste heat in waste heat boilers.

The gas stream from the secondary reformer passes to the shift reaction. This reaction is aided by a promoted iron oxide catalyst. Low temperatures and excess steam favour the equilibrium conversion. In practice a temperature in the range 350–500° C is necessary to give adequate catalyst activity. Typical compositions of gas before and after the shift reaction are:

	Secondary Reformed Gas	*Gas from Shift Reaction*
	% vol.	*% vol.*
CO_2	10·5	17·0
O_2	0·1	0·1
CO	11·5	3·0
H_2	57·0	60·0
CH_4	0·3	0·3
N_2	22·6	20·0



AMMONIA FROM NATURAL GAS BY METHANE – STEAM REACTION
(Design by M.W. Kellogg Company)

The next stage is the purification of this gas stream. The methods involved in this purification are conventional processes common to the production of ammonia from any source. Carbon dioxide was originally removed by scrubbing with water at pressures of 15–20 atmospheres, and this is still commonly practised. Alternative processes include absorption of carbon dioxide by alkanolamines (e.g. in the Girbotol process) and the hot carbonate process. The latter method, by which carbon dioxide is absorbed in potassium carbonate, is the most recent major development in this field and is coming into increasing use. The economics of this operation are improved where carbon dioxide is at high pressure and high concentration. The general observation has been made that consideration should be given to the hot carbonate process when the partial pressure of carbon dioxide in the gas stream is not less than 20 lb/sq in.

The removal of carbon monoxide may be effected either by absorption in 'copper liquor' (consisting of copper ammonium formate, acetate or carbonate), or by the process of methanation. The latter process is used where the carbon monoxide content has already been reduced to a low level. Since it involves the catalytic conversion at high pressures of carbon monoxide with hydrogen to methane and water, it consumes some of the hydrogen, and is only likely to be used in ammonia converter systems using the highest pressure converters.

An alternative approach to the removal of carbon monoxide is the integration within one plant of facilities for methyl alcohol and ammonia synthesis. One method of doing this passes the synthesis gas, after carbon dioxide removal, to a methyl alcohol converter. Here most of the carbon monoxide is consumed, together with some of the hydrogen. Since there will be a residue of carbon monoxide in the gas stream, it is still necessary to use a copper liquor plant to remove carbon monoxide, but obviously most of the load on such a plant will have been eliminated by the methyl alcohol synthesis. The economics of this form of integration are somewhat impaired by the lack of balance of the synthesis gas fed to the methyl alcohol converter, whereby a large converter system is likely to be required for a relatively small production.

So far as ammonia conversion is concerned, petroleum chemical plants can follow any of the established conventional techniques using converter pressures ranging from 100 to 1,000 atmospheres.

Both natural gas and refinery gases are normally available at an elevated pressure. In the operation of the traditional methane–steam reaction, it was necessary to reduce the gas supply to atmospheric pressure, and then to recompress the reaction products. This is clearly illogical and costly. Two approaches have been developed towards the elimination of this economic disadvantage in the traditional methane–steam process. The first was to modify the methane–steam process and the second was to develop an alternative process altogether.

The pioneer plant operating the methane–steam process at an elevated pressure came on stream just before the end of 1953. One of the design problems in establishing such a process had been the development of materials of construction for the tubes of the primary reforming furnace which would withstand the severe temperature conditions at an elevated pressure. The reaction is now commonly carried out at pressures of 3–7 atmospheres.

The effect of increased pressure on the equilibrium of the methane–steam reaction is unfavourable (since two molecules of reactant give four molecules of product), but this is not of major importance where secondary reforming is carried out. In such a case it is common for the exit gases from primary reforming under pressure to contain 6–8 per cent of unreacted methane. This is effectively consumed in the combustion with air involved in secondary reforming. The energy consumed may be partly recovered by a second pass over the reaction catalyst, and also by a waste heat recovery system. The operation of the shift reaction under elevated pressure is quite normal (except for the increased cost of the equipment designed to resist the higher operating pressure), and the process can thereafter follow conventional lines.

The alternative basic process, which was developed at approximately the same time as the methane–steam process under pressure, is that of partial oxidation. The reaction, expressed in terms of methane, is:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2$$

Since dilution of the gases with nitrogen at this stage is disadvantageous in several respects, it is common to use oxygen rather than air as the basis for this reaction. This calls for an air separation unit. Steam is also commonly introduced into the reaction. Where the

hydrocarbon involved in the reaction is a heavy fuel oil, the hydrogen to carbon ratio is much lower than for methane (the mol ratio is rather less than 2 : 1 for a fuel oil against 4 : 1 for methane). In such a case the complete reaction of the carbon present with oxygen to form carbon monoxide will provide more than sufficient heat to raise the reaction mixture to its required temperature. In these circumstances, the addition of steam to the reactants is necessary.

In practice, as usual, a combination of reactions takes place. Important amongst these is the complete and rapid reaction of the oxygen with some of the methane to give carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The carbon dioxide and water will react more slowly with excess methane, to give mixtures of carbon monoxide and hydrogen:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
$$2CH_4 + 2H_2O \rightarrow 2CO + 6H_2$$

The operating conditions in the combustion chambers, or gas generators, may vary appreciably. This derives at least partly from the fact that the process may be applied to almost any hydrocarbon, from methane to the heaviest fuel oils. The temperature is likely to reach about 1,400° C. It is possible to operate the process at atmospheric pressure, but advantage is normally taken of the fact that the reaction can be carried out under pressure, and this may range from 8 to 30 atmospheres. By this means, as has already been indicated, specific advantage can be taken of the frequent availability of refinery gases and natural gas at an elevated pressure. With fuel oil as the raw material it is far more economic to pump the liquid hydrocarbon into the gas generator at an elevated pressure, rather than to effect an equivalent compression of the gaseous reaction products. The use of fuel oil as raw material is likely to require the introduction of some means for the separation and disposal of carbon produced. The conditions of high temperature and carbon deposition do not tend to favour the use of catalysts in this operation.

The shift reaction and carbon dioxide removal may be carried out (still under pressure) by conventional techniques. The final removal of carbon monoxide (together with any residual inert gases) is, in this process, normally effected by a liquid nitrogen wash. By this means advantage can be taken of the air separation unit which provides

oxygen for the partial oxidation reaction. By the use of appropriate conditions in the liquid nitrogen column, carbon monoxide, argon and methane are removed with the liquid nitrogen, whilst the purified hydrogen stream, together with a proportion of evaporated nitrogen, passes out at the top. Further nitrogen is then added to the hydrogen stream to make it up to the correct proportion for ammonia synthesis. This liquid nitrogen wash is a valuable technique where an air separation unit is required for oxygen production, since, although it may require more energy to operate than alternative procedures, it eliminates the necessity for purging the recirculating stream from the ammonia converters, which is otherwise necessary to prevent an accumulation of inert gases, and which involves some loss of raw material. The partial oxidation process for synthesis gas production will lend itself to any of the conventional techniques of ammonia conversion.

A source of increasing interest for ammonia production is the volatile fraction of the gas stream from catalytic reforming units. There is commonly available from a catalytic reformer a fraction comprising 80–95 per cent volume of hydrogen, with methane as the major impurity. Such a stream, if available in sufficient quantity, is clearly valuable for ammonia production. The introduction of nitrogen is a factor which may vary according to specific conditions. It may be convenient to consume the hydrocarbons present in a process akin to secondary reforming, and to introduce nitrogen by this means. If a liquid nitrogen wash is to be employed, it is only likely to prove economic if an application exists for the oxygen from the air separation unit. Methane will be separated from the hydrogen stream in the liquid nitrogen column. The methane may then form part of an additional synthesis gas train operating a partial oxidation process, consuming oxygen. Whatever detailed arrangements are made to suit local conditions, the size and complexity of the purification units are likely to be less with such a concentrated hydrogen stream than with conventional synthesis gas preparation.

The influence of petroleum raw materials on ammonia and fertilizer production has been felt in a variety of ways, amongst which may be noted the following:

(*a*) Owing to the ease of handling raw materials in fluid form, the capital costs of ammonia plants can be reduced.

(*b*) Similarly it is found more simple to operate a truly continuous unit for the production of crude synthesis gas using a raw material in the fluid form.

(*c*) The economics of synthesis gas production from hydrocarbons are generally more favourable than from coke, partly by virtue of the higher concentration of hydrogen in the crude synthesis gas from hydrocarbons. This factor tends to reduce the load on the purification units treating the hydrogen stream.

(*d*) The development of processes based on natural gas has enabled ammonia to be economically produced in countries such as Italy, which have natural gas but no coal resources.

(*e*) The availability of processes based on heavy fuel oil has made the economic production of fertilizers possible almost everywhere, since fuel oil is a basic item of commerce in every country.

The impact of petroleum chemicals in this field has been essentially economic. The world-wide expansion in the use of nitrogen in recent years has been rapid.

The figures for production and consumption (in terms of '000 metric tons N) for the world excluding the U.S.S.R. are as follows:

	Production	*Consumption (total)*	*Consumption (industrial)*
1955/6	8,068	7,552	1,243
1956/7	8,648	8,347	1,370
1957/8	9,493	9,283	1,510
1958/9	10,398	9,957	1,630
1959/60	11,057	10,459	1,715

As can be seen, the preponderant usage of nitrogen (approximately 83 per cent) is for agricultural purposes. In the 1958–59 season the breakdown of synthetic ammonia facilities was quoted as follows (for the world, excluding U.S.S.R.):

Total capacity: approximately 8 million metric tons N

Based on petroleum	55%
Based on coal and coke	40%
Other	5%

Before 1939 over 90 per cent of world ammonia capacity was based on coal or coke. In the U.S.A. the proportion of synthetic ammonia

based on petroleum is normally quoted as about 90 per cent (65 per cent is methane–steam, 14 per cent partial oxidation, and the balance catalytic reformer gas streams), at the present time.

Quoting such figures of capacity, production and percentage applicable to petroleum is subject to the usual hazards due to rapid changes. Global production of nitrogen (including the U.S.S.R.) in 1961–62 is expected to reach nearly 14·3 million metric tons of N, and consumption is expected to rise to 18·2 million tons by 1965. Capacity is rising even faster and will possibly exceed 24 million tons in 1965. A very high proportion of the new capacity will use petroleum as a basis. For example, in Japan, which is a major producer of synthetic ammonia, it is anticipated that reliance upon petroleum feedstocks, which accounted for 47 per cent of production in 1960, will reach 76 per cent in 1963. Some of the additional capacity makes use of by-product hydrogen (e.g. from chlorine cells), and some is based on coal.

There is some tendency for local fertilizer production to represent a sort of national status symbol for emergent countries. This is one factor encouraging the current trend for plant capacity to run ahead of demand.

The techniques indicated (more particularly the methane–steam reaction) represent a means of preparing hydrogen streams for all types of hydrogenation operation, but by far the largest volume of hydrogen is required for ammonia production.

Incidental to the question of the source of raw material for ammonia, the whole fertilizer industry has been exhibiting a number of new trends during this recent period of rapid development. One factor of interest in the application of ammonia as a fertilizer is the direct injection of ammonia or its solutions into the soil and into irrigation water. This is an effective way of fixing nitrogen in the soil without the necessity for making further derivatives from ammonia. These techniques are now widely applied in the U.S.A. and owe their commercial development to petroleum chemical ammonia.

The trend in fertilizers is towards mixtures of high plant nutrient content. This has led, in production terms, to a concentration on such products as ammonium nitrate and urea, and away from ammonium sulphate.

Both ammonium nitrate and urea production units are normally adjuncts to ammonia plants. Ammonia is readily oxidized to nitric

acid, which is then reacted with more ammonia to give ammonium nitrate.

Ammonia plants involve the separation of a carbon dioxide stream from the synthesis gas, as previously described. Frequently this is simply exhausted to atmosphere. Alternatively carbon dioxide may be compressed for marketing in the liquid or solid form. The most satisfactory outlet for this stream, however, is in its reaction with ammonia to produce urea, which is now carried out on a very large scale.

The consideration of the derivatives of ammonia is assumed to be outside the scope of this book.

Methyl Alcohol

The distillation of wood was the original source of methyl alcohol. This source is still exploited on a very limited scale.

The switch to coal as the main source of methyl alcohol was initiated by the Germans, and attained a major commercial significance in the 1920's.

More recently, the trend towards the use of petroleum sources of raw material for synthesis gas has followed a very similar pattern for both ammonia and methyl alcohol. Today in the U.S.A. 99 per cent of methyl alcohol is petroleum-derived.

A minor but significant proportion of methyl alcohol of petroleum origin in the U.S.A. is obtained by the oxidation of higher paraffins. The major developments have been based upon natural gas or refinery light gas streams.

The basic reaction for the synthesis of methyl alcohol is as follows:

$$CO + 2H_2 \rightarrow CH_3OH$$

The crude synthesis gas is treated somewhat differently in this case than in ammonia synthesis. Carbon monoxide is one of the synthesis raw materials, and therefore the shift reaction is not applied. There is of course no requirement in the case of methyl alcohol synthesis for the introduction of nitrogen.

In the manufacture of crude synthesis gas the proportions of hydrogen and carbon monoxide can be varied by an adjustment of the conditions of gas generation. In the methane–steam reaction, for example, the use of excess steam will push the equilibrium in favour of carbon monoxide. A similar effect can be obtained by the recycle

of a carbon dioxide gas stream to the synthesis gas generation stage. By the use of such means the conditions for the manufacture of the crude synthesis gas are adjusted to give an approximate hydrogen to carbon monoxide mol ratio of 2 : 1, as indicated by the synthesis reaction.

According to the conditions of manufacture of the crude synthesis gas, it may be necessary to effect the removal of carbon dioxide from the gas stream before it passes to methyl alcohol synthesis. Some carbon dioxide is commonly extracted for recycle to the reforming furnace.

The hydrogen/carbon monoxide mixture is compressed to 200–350 atmospheres pressure and heated. The gases pass into a copper-lined steel converter, containing a catalyst usually based on zinc oxide (promoted with other metallic oxides such as chromium oxide). The reaction temperature is controlled at about 300° C by the provision of appropriate facilities for heat removal.

The equilibrium reaction is affected favourably by elevated pressures, and adversely by an increase of temperature. The catalysts will operate effectively within the desired temperature range only when the reaction proceeds at high pressures.

Methyl alcohol is condensed out of the reaction products, and the unreacted gases recycled.

There is an alternative reaction which is also utilized in practice for methyl alcohol synthesis,

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

In this case the hydrogen and carbon dioxide will commonly be derived separately, and blended as required for the synthesis. It is possible, for example, to use marginal hydrogen capacity from a synthesis gas unit in combination with a carbon dioxide stream which may also be derived from the same synthesis gas train following the shift reaction. This represents one of the ways of integrating methyl alcohol and ammonia production. In this case, the converter product is an aqueous crude methyl alcohol, containing as impurities, ethyl alcohol, with some ethers and higher alcohols.

Reference has already been made to the integration of methyl alcohol with ammonia production by the use of a methyl alcohol converter to remove carbon monoxide from the gas stream, and by the combination of marginal hydrogen and surplus carbon dioxide from

a synthesis gas unit. Amongst other possibilities, marginal hydrogen can also be combined with a carbon monoxide stream derived from an ammonia plant copper liquor unit as a raw material for methyl alcohol. For these reasons it is common to integrate methyl alcohol production with ammonia production in some way.

The usage in the U.S.A. of methyl alcohol in 1960 was slightly over 2,000 million lb (equivalent to 298 million U.S. gallons). Details of the consumption in 1960, with comparable predictions for 1965 have been quoted as follows:

	1960	*1965*
	million U.S. gallons	
Formaldehyde and inhibitor	125	155
Polyformaldehyde	2	17
Methacrylates	13	20
Methylamines	9	16
Dimethyl terephthalate	10	17
Methyl halides	7	13
Ethylene glycol	16	18
Other chemical uses	20	32
Anti-freeze	10	8
Solvents	20	25
Aircraft fuel injection	17	6
Exports	29	7
Miscellaneous	20	30
	298	364

There is a substantial excess capacity for methyl alcohol in the U.S.A. and this position is likely to continue.

A detailed study of formaldehyde is considered to be beyond the scope of the present book. The substantial basis of production is indicated in the above table. It must be added that methyl alcohol accounts for only 75 per cent of formaldehyde production in the U.S.A., the remainder coming from the paraffin oxidation processes already outlined.

Formaldehyde is normally made by the catalytic oxidation of methyl alcohol. The catalyst commonly comprises silver or copper on an inert support and the temperature is in the range 450–700° C. It is customary to employ a slight deficiency of air for the completion of the oxidation reaction.

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O$$

This causes some formaldehyde to be produced also by dehydrogenation.

$$CH_3OH \rightarrow CH_2O + H_2$$

The second of these reactions is endothermic whereas the first is highly exothermic. Adjusting the conditions so that both reactions take place enables the net reaction to become thermally self-supporting.

An alternative process oxidizes methyl alcohol with a substantial excess of air in the presence of an oxide catalyst consisting of a mixture of the oxides of molybdenum, iron or vanadium.

The major formaldehyde outlet is in a variety of synthetic resins (in combination with phenol, urea, etc.), but it is also important as a chemical intermediate.

Fischer–Tropsch Reaction

This reaction is a catalytic condensation of hydrogen and carbon monoxide, designed to give high molecular weight hydrocarbons, with the elimination of water. The general reactions are:

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$
$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$$

The first reaction represents the production of paraffins, and the second the production of olefins.

The original concept was German, and it was developed with the particular aim of supplementing Germany's petroleum supplies, using coal as a raw material. Subsequent developments have used both coal and natural gas as raw materials. In its modified form, it may now be regarded as a process available for the production of higher hydrocarbons and oxygen compounds from petroleum sources. The economics of such a process in a normal free economy are still in some doubt. The two major projects developed since 1945 have each had a struggle to establish themselves, one in South Africa based on exceptionally cheap coal, and one in Texas based on natural gas (the latter currently shut down).

The U.S. modifications to the original Fischer–Tropsch process have appreciably changed the yield structure. The synthesis, in its original German form, took place preferably at 7–10 atmospheres pressure, at a temperature of 180–200° C, and in the presence of a

cobalt (or sometimes an iron) catalyst. The Hydrocol process (the U.S. modification), using natural gas as the raw material for synthesis gas production, operated the synthesis at 15–35 atmospheres pressure, at 290–375° C, over a finely divided iron catalyst. The resulting yield structures have been compared as follows:

	Fischer–Tropsch in Germany		*Hydrocol in U.S.A.*	
	% wt.	vol. % olefins	% wt.	vol. % olefins
$C_3 + C_4$ stream	10	40	32	82
Naphtha cut	30	26	56	85–90
Gas oil cut	33	8	8	75–85
Residue	27	—	4	—
	100		100	

As can be seen, the Hydrocol process offers a higher yield in the more valuable gasoline range. The C_3–C_4 streams from the Hydrocol process are highly olefinic, and clearly of considerable interest as synthesis raw materials. The yield of waxes is much lower in the Hydrocol process.

There is a considerable production of oxygenated chemicals in the Hydrocol process. These were not worked up to any extent for commercial use by the Germans and they are not produced to any significant extent when using a cobalt catalyst at low pressures. In the water layer separating from the Hydrocol reaction products, are to be found acids (mostly acetic and propionic), aldehydes (mostly acetaldehyde), ketones (mostly acetone) and alcohols (mostly ethyl and n-propyl). These have never been separated in large quantities, but the process remains a potential source of such materials. Some chemicals are being recovered from the South African Fischer–Tropsch plant, but the economics of this whole operation have yet to be demonstrated.

Chapter 12

Petroleum Aromatics

General Economic Factors

In Chapter 3, reference was made to catalytic reforming and Catarole cracking as sources of liquid fractions containing a high proportion of aromatics.

Aromatic hydrocarbons have been raw materials of importance to the chemical industry for many years, and their potential availability from certain petroleum processes has also been obvious for an extended period. Until fairly recently, supplies of major aromatic compounds derived from coal carbonization were sufficient to meet all chemical needs. The economics of separating individual aromatic compounds from petroleum concentrates was frequently then unfavourable, bearing in mind the value of aromatics within the petroleum industry as components of automotive and aviation fuels.

The position has been gradually changing over a number of years. In the U.S.A. a substantial proportion of the total toluene and xylene availability has been recovered from petroleum sources for some considerable time. as indicated by the following table, quoting aromatics production in '000 U.S. gallons.

	BENZENE		TOLUENE		XYLENE	
	Coal	*Oil*	*Coal*	*Oil*	*Coal*	*Oil*
1952	216,000	35,500	64,000	41,000	10,000	61,500
1954	165,000	92,000	36,000	123,000	10,000	100,000
1956	225,000	112,000	43,000	131,000	12,000	124,000
1958	144,000	142,000	32,000	207,000	9,000	191,500
1960	140,000	309,000	33,500	240,000	8,500	274,000

This table exhibits the even more significant trend of U.S.A. benzene production, whereby the proportion from petroleum has been growing very substantially during the past few years.

The position is governed by economic factors, and more particularly by the factor of availability. Benzene, toluene and xylenes are

available from coal to the extent that coal is carbonized. This, in turn, is related to the progress of the steel and gas-making industries. These industries are not expanding in line with the demand for aromatic hydrocarbons, and the position is further aggravated by improvements in technique, which have the cumulative effect of requiring less coal to be carbonized per unit of production in these industries.

It is not necessary, in most cases, to recover the aromatics from coal carbonization, and in some instances it may be preferable to leave some aromatic compounds in the gases from coal carbonization, where they have some value as fuel, rather than undertake the cost of their recovery. In the petroleum industry the capacity for producing aromatic concentrates is also in existence. Circumstances can arise whereby these facilities are marginally surplus to petroleum requirements. The trend to jet aircraft engines, for example, is reducing the demand for aviation gasoline. In these circumstances, it will readily be seen that economic factors can tend to favour the flexibility of the petroleum source.

Outside the U.S.A. the trend to petroleum-based aromatics is not yet so marked, but the movement is in the same direction. The individual separation of the xylene isomers, for example, is normally based on petroleum xylene concentrates. Relatively little of the benzene used in the chemical industry outside of the U.S.A. has so far been of petroleum origin.

The appearance of the technique of hydrodealkylation (discussed later in this chapter under 'Production Techniques') is likely to accelerate the global trend towards the derivation of aromatics from petroleum, and it is already adding naphthalene to the list of aromatic products so made.

Recovery Processes

The recovery of aromatic compounds from the concentrates produced in such operations as catalytic reforming may be achieved by a variety of alternative techniques considered separately below.

The recovery and separation of petroleum aromatics offers a spendid illustration of the various techniques (some of which were outlined in Part One of this book) available for product separation. One aspect of this problem is represented by the separation of the

aromatic compounds from the non-aromatics. A second aspect is the separation of the aromatic compounds from each other. A particular instance of the latter case arises from the recent development of commercial requirements for each of the xylene isomers.

(a) *Fractional Distillation*

This can seldom be used alone for the separation of pure compounds, but may be applied to the preparation of narrow-distillation-range concentrates. Not only are the aromatics difficult to separate in a pure form by virtue of the presence in the same fraction of other hydrocarbons with very similar boiling points, but they also have a tendency to form azeotropes with certain paraffins and naphthenes.

It has, however, proved possible to separate pure toluene by the fractional distillation of a concentrate prepared by subjecting an appropriate fraction to two cycles of catalytic reforming.

Fractional distillation is, of course, frequently used in conjunction with the other separation processes.

(b) *Extractive Distillation*

This process involves distillation in the presence of a solvent which becomes the least volatile component of a mixture. The solvent is selected to produce an increase in the relative volatility of the components to be separated. Requirements for a satisfactory solvent include: non-corrosivity to equipment, non-reactivity with feed components, thermal stability, high selectivity and a higher boiling point than feed components (to enable ease of separation from them). A suitable extractive solvent for benzene or toluene recovery is phenol.

From a catalytic reformate, the benzene and toluene concentrates are first separated by a primary distillation. Each concentrate is given a separate extractive distillation with phenol to remove non-aromatics. The derived benzene fraction is treated with sulphuric acid, washed with sodium hydroxide and water, purified by distillation, and dried. The derived toluene fraction is treated with maleic anhydride, washed with sodium hydroxide and water, and dried.

(c) *Azeotropic Distillation*

This involves distillation in the presence of a solvent which becomes the most volatile component of a mixture. The solvent is selected, as

in extractive distillation, to produce an increase in the relative volatility of the components to be separated. The choice between azeotropic and extractive distillation is an economic one, depending upon the concentration of aromatics in the feed. Azeotropic distillation is generally favoured for a feed containing upwards of 40 per cent aromatics. The main difference in practice is that in azeotropic distillation the added agent goes overhead with the non-aromatics, whereas in extractive distillation it mostly goes with the aromatics as column bottoms.

Azeotroping agents which have been found effective include methyl ethyl ketone and water in combination, methyl alcohol, and nitromethane.

(d) *Solvent Extraction*

The selectivity of the solvent chosen for aromatics in the presence of non-aromatics, should be such that a two-phase system is obtained at a convenient temperature, and that the phases should separate easily. The solvent should also be non-corrosive, non-reactive and thermally stable.

Amongst the traditional solvents used for the separation of aromatics from petroleum fractions are sulphur dioxide and furfural. In modern practice, where the main purpose of the operation may be the recovery of the aromatics as pure compounds, probably the commonest technique is the Udex process, using aqueous diethylene glycol as the solvent. After the extraction, the mixture of aromatics is passed through a contact clay treater, and then to a distillation train, where benzene, toluene and the xylenes are recovered in separate columns.

A recent development takes a C_8 concentrate from catalytic reforming and Udex extraction, containing 25–30 per cent of ethyl benzene, and subjects it to a very close fractionation—a process known as superfractionation. This is achieved in a 600-foot column (comprising three sections of 200 feet each) containing 350 plates. The aim of this operation is the recovery of pure ethyl benzene, and a product purity of 99·7 per cent is claimed.

(e) *Solid Adsorption*

The selective adsorption of aromatics on silica gel is employed in the Arosorb process. The adsorption in the silica gel bed proceeds to

about 70 per cent saturation. Non-aromatics are washed from the bed with a volatile paraffin, such as butane, and the aromatics are then extracted by a stream of xylene. Benzene and toluene are then purified by distillation.

(f) *Crystallization*

The boiling points of the xylene isomers and of ethyl benzene are all close together, and it is particularly difficult to separate the meta- and para- isomers. On the other hand, the freezing points of these compounds show a much wider spread.

The mixed xylenes are dried over activated alumina, and then cooled. Waiting tanks allow the p-xylene crystals to grow to a size convenient for separation in a centrifuge. These crystals are melted and recrystallized. The crystals are again separated and liquor from the second centrifuge (containing 40–50 per cent p-xylene) is recycled to feed. The recovery of p-xylene is limited in practice by interference from eutectic formation to about 60–70 per cent, as a 95 per cent pure product.

The recovery of p-xylene may be improved by allowing it to form an equimolar compound with carbon tetrachloride, since the other xylene isomers do not form such adducts. This simplifies the separation by crystallization, more particularly by minimizing the interfering effects of eutectics. It is possible to increase the total recovery of p-xylene to about 90 per cent in this way. It is also possible to recover m-xylene in a pure form if there should be an outlet for it.

Octafining is a catalytic isomerization process which brings the relative concentrations of the C_8 aromatics in a mixture towards an equilibrium value. It may be used in conjunction with the crystallization techniques for separation of xylene isomers. For example, after the removal of p-xylene by crystallization, the filtrate (containing 7·9 per cent p-xylene) can be treated at 400–500° C and 10–25 atmospheres in a reactor using a catalyst comprising platinum on a silver–alumina support in the presence of hydrogen. The isomerization which takes place brings the p-xylene content of the mixture up to 19 per cent. The isomerizate is cooled, hydrogen separated, and aromatics below and above C_8 removed by fractionation. The remaining C_8 fraction is returned to the crystallization process for separation of further p-xylene.

Production Techniques

In the past year or two there has been a minor revolution in petroleum aromatics, occasioned by the arrival of the processes of hydrodealkylation. The principle, in brief, is to treat an alkyl aromatic with hydrogen to produce the aromatic compound together with a paraffinic hydrocarbon. Catalytic and thermal processes are available.

In commercial terms, the major developments are the production of naphthalene from alkylnaphthalenes (present in refinery cracking recycle streams), and the production of benzene from toluene, or higher homologues.

Until recently, the economics of recovering naphthalene from petroleum fractions were not favourable, since supplies of naphthalene from coal tar sources have usually been adequate. The new processes have appeared at a moment when the prospects of a certain stringency in naphthalene supplies in the U.S.A. are being taken seriously. Commercial naphthalene production on this basis began in the U.S.A. in 1961, and is likely to provide a significant factor in U.S. naphthalene supply in the future. The position is also being closely studied in Europe, where the prospects of a shortage of coal tar naphthalenes are not so obvious.

The development of capacity for producing benzene from toluene is an illustration of simple economic factors. Benzene and toluene are each available on a very substantial scale, both from coal tar and from petroleum. Whilst there is a keen demand for benzene as a chemical intermediate, toluene has only limited chemical uses. The value of toluene is, therefore, currently lower than that of benzene, to such an extent that it is economic to build a hydrodealkylation plant consuming toluene and producing benzene. If too many people build such plants (as seems a real possibility in the U.S.A. at present) the price of benzene may be forced down by over-production, while simultaneously that of toluene is increased by greater usage, to the point at which the conversion is scarcely economic.

Usage of Aromatics

Benzene has for a long time been a major organic chemical intermediate, and the variety of its applications is indicated by the following table of consumption in the U.S.A. in 1960.

	Million gallons
Styrene monomer	219
Phenol	102
Nylon	37
Synthetic detergents	34
Aniline	13
DDT	16
BHC	2
Maleic anhydride	10
Mono- and dichlorobenzene*	11
Nitrobenzene†	2
Miscellaneous	22
Exports	23
Total	491

* Other than for making phenol.
† Other than for making aniline.

In the United Kingdom the total benzene production for chemical use is of the order of 450 million lb, and the contribution of petroleum is relatively small. In France in 1959 20 million lb out of a total production of 260 million lb of chemical benzene were of petroleum origin. The pattern of benzene usage in France is expected to vary according to the following figures (as millions of lb).

	1959	*1965*
For styrene	76	210
For phenol	89	140
For cyclohexane	20	80
For synthetic detergents	28	47
Miscellaneous	67	123
	280	600

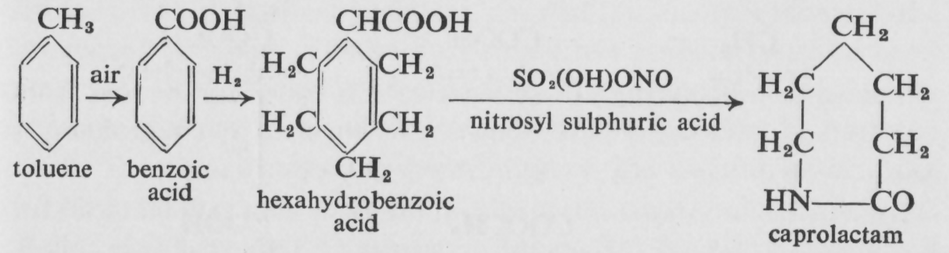
It is most unlikely that an increase of this order can be met from coal sources, and some development of benzene from petroleum is clearly probable in France within the next year or two.

Toluene has occupied a less important place as a raw material for the chemical industry. Its usage conforms to the following U.S. pattern:

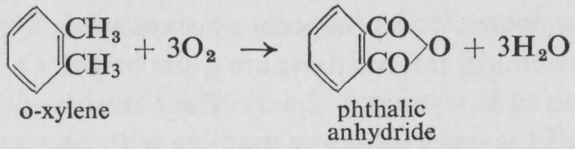
Motor fuel	24%	Explosives	8%
Aviation gasoline	25%	Chemical synthesis	11%
Solvent purposes	11%	Exports and miscellaneous	21%

In certain spheres, the prospects of expanding consumption of toluene as a chemical intermediate are quite bright. One of these is in the production of isocyanates. 2,4-Tolylene diisocyanate (formed by the reaction of the corresponding diamine with phosgene) is a major raw material in the production of polyurethane resins. It contains a proportion of the 2,6-isomer. The resins are produced by the interaction of a diisocyanate with an appropriate polyester, or more commonly, polyether. Such resins form the basis of the 'plastic foam' used widely today for cushioning in furniture and transport vehicles. A big future is also predicted for the comparable rigid foam in various forms of lightweight construction.

Another contender for increased toluene usage is the Snia Viscosa route to caprolactam. Caprolactam is the monomer for nylon 6, which is expanding today at an even greater rate than the more conventional nylon 66. There is only a limited commercial application of the Snia Viscosa route so far, but several plants are planned. The first stage of this process is the oxidation of toluene by air in the liquid phase to benzoic acid, using a catalyst system which may either consist of bromine-promoted manganese salts or ketone-promoted cobalt salts. The next stage is the hydrogenation of benzoic acid to hexahydrobenzoic acid. The catalyst for the hydrogenation is chlorine-free palladium or platinum black, and the reaction can be effected in alcohol solution. Hexahydrobenzoic acid is reacted with nitrosyl sulphuric acid in the presence of oleum. The operating temperature is 55–65° C, and the reaction continues until the evolution of by-product carbon dioxide ceases. The nitrosyl sulphuric acid is formed by an exothermic addition reaction of sulphur dioxide with fuming nitric acid.

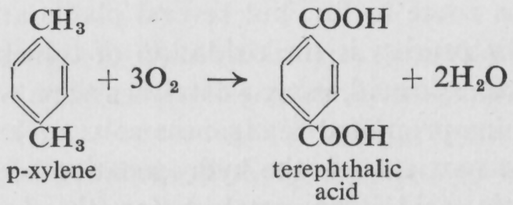


The xylenes have developed extensively as chemical raw materials in the past few years. The first isomer to achieve commercial significance was o-xylene. This may be separated from the other isomers by distillation, and is oxidized to phthalic anhydride.

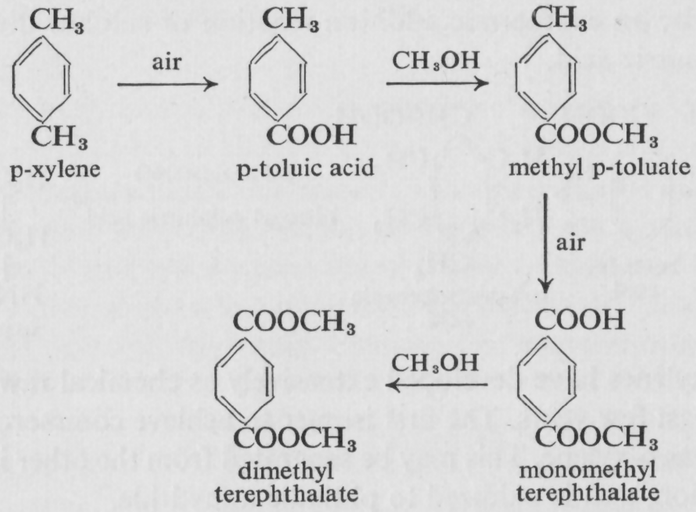


The oxidation takes place in the vapour phase over a vanadium pentoxide catalyst at over 550° C. This process accounts for rather less than 10 per cent of U.S.A. phthalic anhydride. The increasing availability of o-xylene is causing the process to be examined closely elsewhere.

Reference has already been made to the separation of m-xylene and p-xylene. This requirement arose from the use of p-xylene as a raw material for terephthalic acid. p-Xylene may be oxidized under pressure, using nitric acid at 150–250° C. Alternatively, a direct oxidation by oxygen can be employed in the presence of a metal catalyst and a bromine activator.

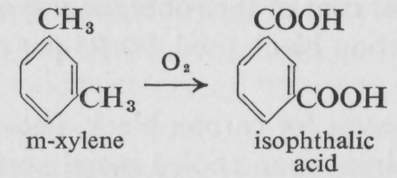


An alternative approach begins with the oxidation of p-xylene with air to give p-toluic acid, which is converted to the methyl ester. Methyl p-toluate is then oxidized with air to monomethyl terephthalate, and the latter is then fully esterified with more methyl alcohol.



Whatever the process, the ultimate product of this synthesis is dimethyl terephthalate. This is reacted with ethylene glycol to provide polyester fibres such as Terylene and Dacron.

The normal C_8 aromatic concentrate (such as may be prepared, for example, by catalytic reforming and Udex extraction) contains more m-xylene than any of the other isomers. Until recently m-xylene had no applications as a chemical intermediate. The production of isophthalic acid from m-xylene has now been developed as a commercial process. This uses liquid phase air oxidation at 300–350° C and 150 atmospheres pressure in the presence of an aqueous solution of ammonium sulphate and ammonium polysulphide.



Isophthalic acid produces esters with properties generally similar to those of the phthalates, so that isophthalic acid enters into competition with phthalic anhydride.

A further development of the oxidation processes, now in commercial operation, endeavours to deal with the problems of separating xylene isomers in a novel way. The mixture of xylenes is oxidized with air in acetic acid solution, at about 15–30 atmospheres pressure and 200° C, in the presence of polyvalent metal salts and bromides as activators. This requires the products of oxidation to be separated instead of the xylene isomers. This separation seems to be proving quite a problem in practice.

The evaluation of prospects for petroleum-based naphthalene in Europe poses quite a few problems, as must be clear from some of the foregoing comments. Firstly, the competitive position must be compared with that of coal tar naphthalene. The prospects of o-xylene as a competitive raw material for phthalic anhydride must be borne in mind. There is always the possibility of the isophthalates from m-xylene taking a share of the phthalic anhydride market. It is, of course, also necessary to predict a future for the alkyd resins and phthalate plasticizers which, by constituting the bulk of the present phthalic anhydride usage, represent the major indirect markets for naphthalene.

Chapter 13

Carbon Black

The subject of carbon black is almost a study in itself. Carbon black consists essentially of fine carbon particles, semi-graphitic in structure. The importance of this commodity may be indicated briefly by stating that 30–35 per cent of the rubber in a tyre consists of carbon black. Of all the carbon black used, 90–95 per cent goes into some form of rubber.

In the channel process for carbon black, natural gas is burned so that the flames impinge upon cooled metal surfaces (commonly of 8–10 inch channel iron). Carbon black collects on the cold surface, and is removed by scrapers into large hoppers. The black is then screw-conveyed into a pneumatic conveyor, which carries it via a grit separator to a cyclone collector. The black at this point has an apparent density of 4 lb/cu ft. Where the black is to be used in the ink industry, the density is increased by agitation to about 12 lb/cu ft, but where it is destined for the rubber industry it is pelletized (using either a wet or a dry process) to an apparent density of 20–25 lb/cu ft (for more economical storage and handling).

The thermal process is based on the straight thermal decomposition of an appropriate raw material, which is normally natural gas. The furnaces operate on a cyclic basis. Refractory bricks are heated to 900–1,400° C during the heating run, and the feed gas is then admitted. The make of carbon black continues until further heating is necessary. The gases from the cracking operation convey the thermal black to a separating system, comprising cyclone separators and bag filters. The filtered gas may then be recycled to operate the heating run of the furnace cycle. Since the recycle gas consists mostly of hydrogen, it may be used for other chemical purposes, including ammonia production. The thermal black is a much coarser product than channel black. Having a much lower reinforcing effect as a result of its coarser particle size, thermal black has somewhat limited applications in the rubber industry.

The furnace process was originally developed on the basis of a natural gas feedstock. This comprises a combined partial oxidation and cracking process taking place at temperatures of the order of 1,300° C. The carbon is formed in the furnace, and carried by the gas flow to a quench tower, where the temperature is reduced to about 200° C by a water quench. The black is collected in a system comprising electrostatic precipitators, cyclone separators and bag filters. The significance of this process derives from the yield of carbon black, which, per unit of natural gas, is nearly twice that of the channel process. The product is slightly coarser than channel black.

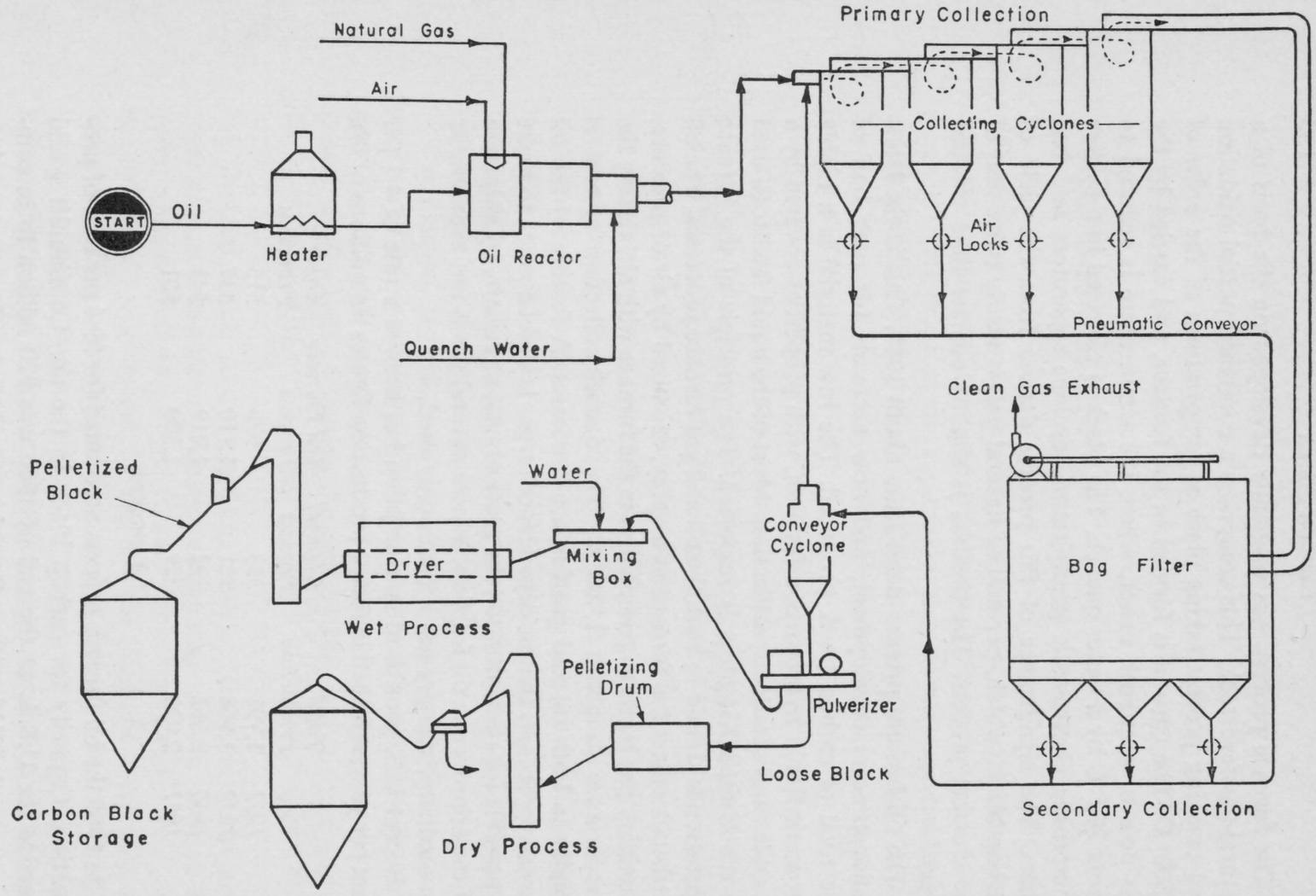
The oil furnace process dates from about 1945. This is the latest major process development, and now accounts for over half of the total of carbon black produced. The raw material is a highly aromatic liquid hydrocarbon fraction, with properties covered by a complex and detailed specification. Most of the liquid feedstock used in the United Kingdom is imported. The principle of the furnace operation is similar in both the oil and gas furnace processes. The oil feedstock enters the furnace as a spray, atomized by air or pressure. Auxiliary gas burns to completion in the furnace with air, raising the temperature to about 1,400° C. The quench-collection system is similar in both oil and gas furnace processes. A feature of the oil furnace process is that its dependence on gas is slight enough to make it possible for operation to take place almost anywhere, by shipment of the appropriate oil fraction. Where natural gas is not available as an auxiliary, refinery gas is commonly used.

Recent U.S. growth of consumption has been at a rate of 4·1 per cent per year, reflected in recent production figures (in millions of lb).

Year	*Total Production*	*Channel Process*	*Oil Furnace Process*	*Other Processes*
1957	1,798	358	926	515
1959	1,968	321	1,110	537
1960	2,052	292	1,219	541
*1961**	2,030	229	1,300	501

* Estimated.

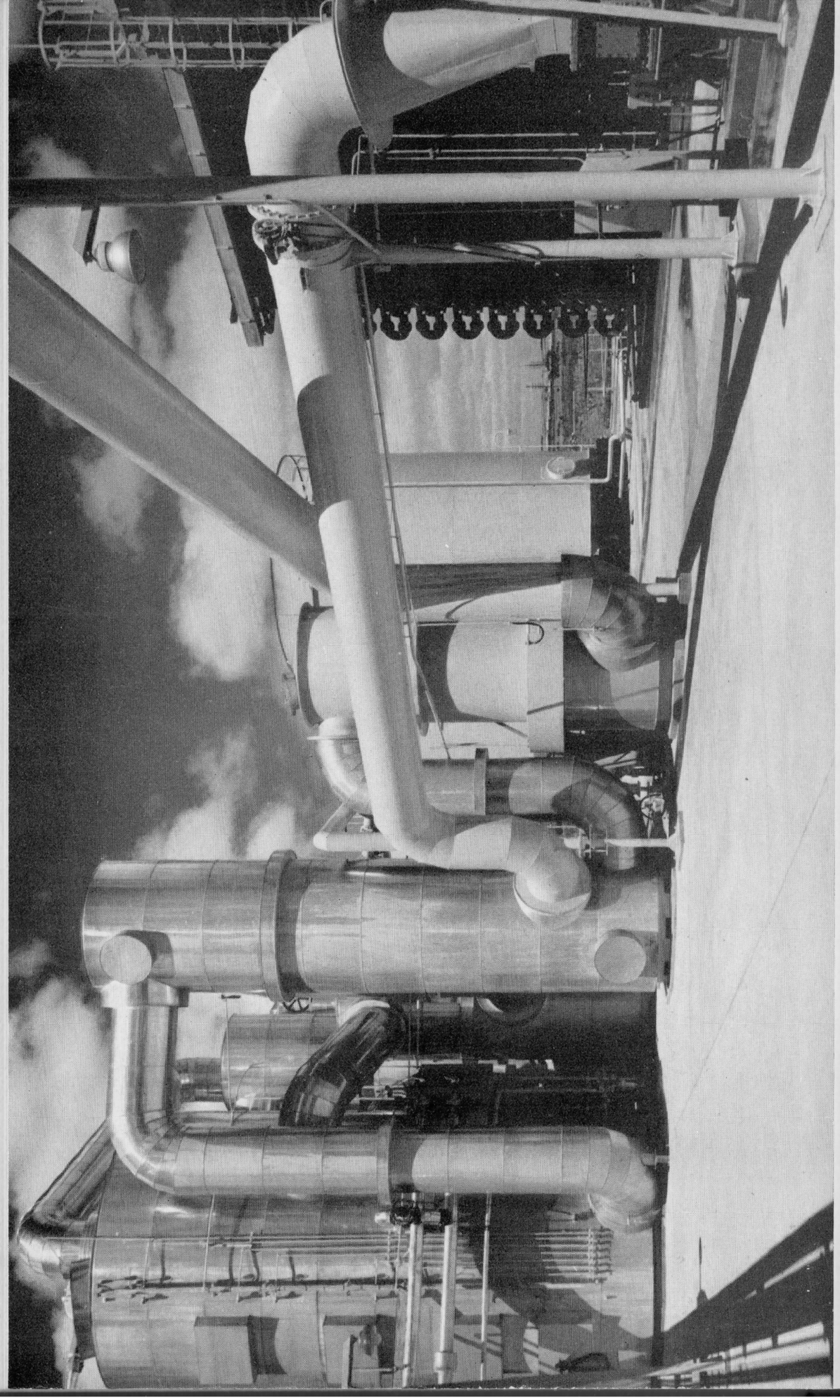
In 1960 the oil furnace process accounted for 59·4 per cent of production. Capacity for carbon black in the non-Communist world outside the U.S.A. at the end of 1960 was 920 million lb in comparison with 2,415 million lb within the U.S.A. The consumption



CARBON BLACK BY OIL FURNACE PROCESS (Design by Continental Carbon Company)
illustrating alternative wet or dry process for pelletizing.

(*Top*) Channel black plant at Skellytown, Texas
(*Bottom*) Oil furnace black plant at Sarnia, Canada
The bottom picture shows the vast improvement in cleanliness of today's oil furnace black plants compared with a typical channel black plant

Courtesy Cabot Corporation



This modern sulphuric acid plant at Geelong, Australia, uses refinery hydrogen sulphide as its raw material

Courtesy Shell Chemical (Aust.) Pty. Ltd.

growth rate outside the U.S.A. is 10·8 per cent per year, and capacity is rising rapidly to take care of this. Production in the United Kingdom in 1960 was approximately 135,000 long tons.

Channel black has been losing its share of the market largely on economic grounds. It is wasteful of raw material, and the process is, incidentally, very dirty to operate. The channel blacks were superior to early furnace blacks in the reinforcing and abrasion-resistant properties which they could impart to the tyre rubber. The more recent oil furnace blacks, in combination with synthetic rubber (SBR grade), have given outstanding road wear characteristics to tyre treads. Other types of black are used where ease of processing is more important than the reinforcing effect, e.g. for rubber mountings and for moulded and extruded goods.

Only a few years ago virtually the entire carbon black industry was centred in the U.S.A. There are now plants in many European countries, Canada and Australia. Further plants are planned in African, South American and Asian countries. Almost all of the new plants are based on the oil furnace process.

Chapter 14

Cyclic Compounds

In dealing with the wide range of products coming under this heading, it is necessary to be selective in picking out the relatively few materials which, as chemical entities, have achieved some measure of industrial significance in the petroleum chemical field.

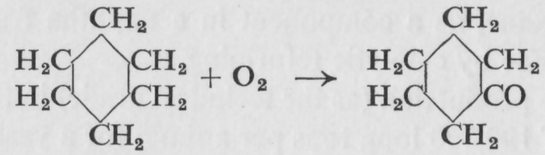
The three headings below provide a brief consideration of some industrially important products and product groups with a cyclic structure, whose fields of interest are strikingly varied.

Cyclohexane

The major significance of cyclohexane, as a separate chemical entity, is its use as a raw material in the production of adipic acid. Not only is adipic acid one of the two major raw materials for the production of nylon 66, but it also represents a step in one of the routes to hexamethylenediamine, which is the other major raw material for nylon 66.

Cyclohexane from petroleum sources is commonly prepared as a concentrate from natural gasoline by fractional distillation. By the standards of chemical products, it is relatively impure. The technical grade may contain 80 per cent cyclohexane, 5 per cent methylcyclopentane and 15 per cent of paraffins, aromatics, etc. Pure cyclohexane may be produced by the hydrogenation of benzene.

Whilst it is possible to oxidize pure cyclohexane to adipic acid in one step, the relatively impure cyclohexane, which is the commonly available grade, is normally oxidized in two steps. The first oxidation is with air at 125–160° C and 3–18 atmospheres pressure in the presence of cobalt naphthenate, to produce cyclohexanone (with cyclohexanol). This is a liquid phase reaction, and during the oxidation two layers form. The upper hydrocarbon layer is recycled and the lower water layer drawn off, retaining a uniform level in the reactor by control of the feed rate.

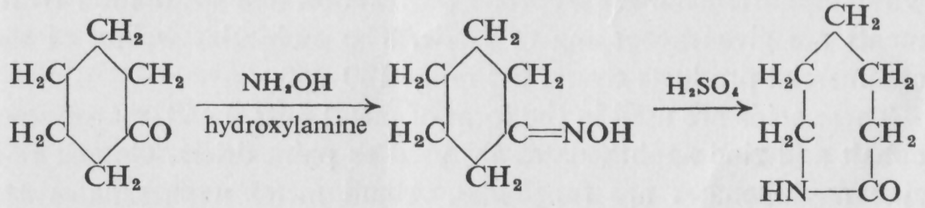


cyclohexane cyclohexanone

A mixture of cyclohexanone and cyclohexanol is separated from the hydrocarbons by distillation. The mixture is treated with nitric acid over a copper–vanadium catalyst at about 80° C, and under elevated pressure. The reaction mixture is chilled to 5° C, and the crystals of adipic acid forming are separated by centrifuging.

$$\underset{\text{cyclohexanone}}{C_5H_{10}CO} + 1\tfrac{1}{2}O_2 \rightarrow \underset{\text{adipic acid}}{HOOC(CH_2)_4COOH}$$

The adipic acid is nearly all used for nylon 66. The major alternative form of nylon is called nylon 6. This is already the leading form of nylon in Europe, and it is entering the phase of rapid expansion in the U.S.A. In the case of nylon 6, the adipic acid and hexamethylenediamine are replaced by the single monomer caprolactam. There are several processes for caprolactam manufacture, and the main ones start from cyclohexane, phenol or toluene. Both the cyclohexane and phenol processes proceed via the production of cyclohexanone. The cyclohexanone is treated at 20° C with hydroxylamine sulphate. The mixture is neutralized with ammonia. The products from the batch reactor pass to a separator where cyclohexanone oxime settles out as an oily liquid. The crude product containing 4–5 per cent water is subjected to the Beckmann rearrangement by treatment with concentrated sulphuric acid at below 140° C. The solution containing caprolactam is continuously withdrawn from the system, and promptly cooled to below 75° C to avoid hydrolysis. It is then cooled further, and neutralized with ammonia. The caprolactam is finally recovered by distillation or by solvent extraction with benzene.



cyclohexanone cyclohexanone oxime caprolactam

About 90 per cent of chemical cyclohexane is consumed in the production of nylon. This does not take into account the reaction by

which cyclohexane, as a component in a naphtha fraction, is converted to benzene by catalytic reforming.

Cyclohexane production (as the technical grade) in the U.S.A. was of the order of 190,000 long tons per annum for a year or two up to 1959, since when there has been a rapid rise to nearly 350,000 long tons in 1961.

Cyclopentadiene

Cyclopentadiene is found in the C_5 fraction obtained in the vapour phase cracking of naphtha, and also in the light oils derived from coal carbonization. Cyclopentadiene can readily be separated by the ease with which it can be dimerized. The dimer can readily be depolymerized back to cyclopentadiene.

Cyclopentadiene has achieved some importance as a raw material for insecticide manufacture. It undergoes a complex Diels–Alder reaction with acetylene and hexachlorocyclopentadiene to give aldrin. Dieldrin is the epoxy derivative of aldrin. The aldrin–dieldrin range of insecticides, mostly made in the U.S.A. and Holland, have world-wide applications for a wide range of pests.

Naphthenic Acids

Naphthenic acids occur naturally in crudes from certain areas (notably Venezuela, Trinidad and California). They are carboxylic acids of substituted cyclopentanes and cyclohexanes, with a wide range of molecular weight from 114 upwards.

The acids of major commercial importance are separated from gas oil fractions in the boiling range 200–370° C. They are extracted with dilute sodium hydroxide solution, and regenerated by acidification with sulphuric acid. Appropriate purification and distillation treatments are given according to grade. The molecular weight of the commercial products covers the range 180–350.

These acids are used in the form of metal salts. Lead, manganese, cobalt and zinc naphthenates are used as paint driers. Copper and zinc naphthenates are fungicides. Alkali metal naphthenates are specialized emulsifying agents. Calcium, barium and magnesium naphthenates are used as fuel oil and lubricating oil additives.

Chapter 15

Sulphur and Sulphuric Acid

Traditional sources of sulphur have been the elemental sulphur recovered by the Frasch process from the domes of the U.S.A. Gulf Coast, and pyrites from a variety of sources. Pyrites is economic only in reasonably close proximity to its source, and the majority of the sulphur entering world trade has been in the form of the Frasch product. This process melts the sulphur underground with hot water, and the molten sulphur is blown to the surface with compressed air. There was a critical period in 1950–52 when it was believed that this source of sulphur was to be very short lived. Since that time, the resources of Frasch sulphur have increased to a marked extent, including the discovery of important new deposits in Mexico. The period of doubt stimulated investigation into alternative sources of sulphur, and it was found to be economic in a number of cases to recover sulphur from refinery gas or natural gas. Where hydrogen sulphide is present in such gas streams, it is frequently necessary in any case to remove it before the gas can be used for fuel or chemical synthesis. The separation is normally effected by amine absorption, from which a concentrated stream of hydrogen sulphide can subsequently be released. This could be a source of air pollution, and it is consequently a happy solution if it is economically feasible to recover sulphur from it.

The recovery of sulphur from hydrogen sulphide is a well-established chemical process,

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$
$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Hydrogen sulphide is first burned with air (and some provision, such as a waste heat boiler, is made for recovering the heat of reaction). The sulphur dioxide formed in this reaction is mixed with an appropriate volume of the original hydrogen sulphide stream and passed through a converter (or Claus kiln) containing an activated bauxite

catalyst. The gases enter the converter at 250–400° C and leave at 400–500° C. The converter effluent is cooled, and liquid sulphur condensed out is pumped to storage. Unconverted gases are passed to a second converter operating at somewhat lower temperatures. Various modifications exist, centred around the same principle, and usually differing mainly in the techniques used for heat recovery.

Some recovery of sulphur from sour natural gas has been carried out for a number of years. The past year or two has seen tremendous development, particularly in Canada and France, in the treatment of sour natural gas. Projects in hand will lift the production of recovered sulphur by this process to something over 2 million tons per annum, and long-term predictions quote figures a good deal higher than this.

Since most of the recovered sulphur is ultimately used to make sulphuric acid, it might seem that an economically attractive alternative would be to make sulphuric acid directly from the hydrogen sulphide stream. The main drawback is that it is economically worthwhile to produce and consume the acid only where the hydrogen sulphide stream is available, since the economics of transportation would always favour sulphur. From a process point of view, the combustion of hydrogen sulphide involves the complication that water is produced as well as sulphur dioxide.

One method of treating the wet sulphur dioxide gases involves drying them before they pass to the converters. The gases from the combustion may be partly cooled in a waste heat boiler, but the outlet temperature must be high enough to prevent the condensation of acid in the boiler. The gases are next cooled in a cooling and scrubbing section, which eliminates any dust present. Cooling the wet gas causes the formation of a substantial volume of acid mist from the water and sulphur trioxide present. The acid mist is removed in an electrostatic precipitator. Air is then introduced and the gases pass to a drying tower, where the drying agent is commonly 93 per cent sulphuric acid. The conversion–absorption system is largely on the same lines as for a conventional sulphur-burning contact plant. The essential difference is that the dried gases must be raised to conversion temperature, before entering the first stage of the converter, by heat exchange with gases from the later stages of the converter.

A more recent development in plants burning hydrogen sulphide

permits the elimination of much of the purification section. The gases from the combustion furnace are partly cooled in a waste heat boiler. The temperature of the gases leaving the boiler is adjusted, so that when they are mixed with sufficient air to dilute the sulphur dioxide concentration to 7·5 per cent, the resultant mixture is still hot enough for the preheating available from the reaction in the first layer of converter catalyst to raise its temperature to about 438° C. The gases then pass through the converter in the normal manner, and proceed directly to an absorber at about 438° C, where the sulphur trioxide is absorbed in 98 per cent sulphuric acid. Sulphuric acid mist is formed in the gas stream, so that gases leaving the absorber are treated in an appropriate type of mist scrubber. This type of plant cannot produce an acid of concentration greater than 93–94 per cent, in view of the moisture content of the gas stream.

Part 3

The Industrial Pattern

Chapter 16

Industrial Influence of Petroleum Chemicals

Some indication of the range of activities directly associated with the chemical industry is given by the classification of official statistics. The statistics of the Board of Trade in the United Kingdom, for example, quote a category described as Chemical and Allied Industries, which includes the following: general chemicals, plastics, coal tar products, dyes and dyestuffs, paints and varnishes, drugs and pharmaceuticals, toilet preparations, fertilizers, disinfectants, polishes, soap, candles and glycerine, and explosives.

Many other process industries are extensive users of chemicals. As examples one may quote the rubber, paper, textile, food, petroleum and transportation industries.

There are certain industrial sectors where the influence of petroleum chemicals has been particularly marked. The industrial applications of specific products have been outlined in earlier chapters. This chapter examines the position from the point of view of some of the user industries. A selection of such industries for consideration must, to some extent, be arbitrary, though certain industries select themselves. The industries considered in this chapter will help to explain the rapid expansion of petroleum chemicals, since each has grown remarkably in recent years.

Plastics

The biggest plastics industry is in the U.S.A. and its record of growth during the past ten years may be summarized as follows:

Year	*Production* (million lb)
1951	2,400
1956	4,000
1958	4,500
1960	6,282

A rough comparison between different countries is illustrated by the following production statistics for 1960:

Country	*Production* (million lb)
U.S.A.	6,282
Italy	660
France (1959)	550
United Kingdom	1,250

In distinguishing the various products in the plastics industry figures for the U.S.A. may be regarded as broadly typical. The breakdown of U.S. production in 1960 was as follows:

	(million lb)
Cellulose plastics	143
Phenolic and other tar acid resins	649
Urea and melamine resins	399
Styrene resins	1,062
Vinyl and vinyl copolymer resins	1,203
Alkyd resins and rosin modifications	628
Coumarone-indene and petroleum polymer resins	265
Polyester resins	190
Polyethylene resins (high pressure)	1,112
Polyethylene resins (low pressure)	225
Polypropylene resins	41
Epoxy resins	66
Miscellaneous	299
	6,282

The plastics industry has, to a considerable extent, grown up in conjunction with the development of petroleum chemicals, and the two have many links. The association is perhaps most obvious in the field of polyolefins, which have been the most rapidly growing, and are now the largest segment of the U.S. plastics industry. This production, throughout the world, is almost exclusively based upon olefins of petroleum origin.

The styrene resins represent another group in which petroleum chemical interest is paramount. Although it may be claimed that much of the world's benzene is still derived from coal, not only is the ethylene a petroleum derivative, but the alkylation process is typical of this field in conception and technique.

The vinyl resins are most commonly based upon acetylene from

coal. A substantial proportion of U.S. vinyl chloride, and significant quantities elsewhere, are, however, based upon ethylene.

The three groups of resins to which reference has been made are those which are produced in the largest quantities in the U.S.A. and, almost certainly, in the world as a whole. An indication of the fields of application of these materials in the United Kingdom has been quoted as follows:

Polyvinyl chloride	
Film	24%
Wire coating	17%
Fabric coating	10%
Extrusions	10%
Other	39%
Polyethylene	
Moulding	34%
Film	30%
Cables	12%
Bottles	9%
Other	15%
Polystyrene	
Refrigerators	27%
Packaging	19%
Electrical (radio, TV)	13%
Housewares	12%
Toys	10%
Other	19%

Another group which falls into a distinctive category includes the phenolic, alkyd, urea and melamine resins. The major raw materials for this group include phenol, formaldehyde, glycerine, phthalic anhydride, urea and melamine. If we bear in mind that over 80 per cent of organic chemicals in the U.S.A., about 50 per cent in the United Kingdom and over 30 per cent in Western Europe are of petroleum origin, it is clear that any major industry, based specifically on such organic chemicals as its raw materials, will also trace much of its origin back to petroleum.

A further group is exemplified by the cellulosics, where the fundamental raw material is of natural origin. In such a case synthetic chemicals make their contribution as processing products. It may be expected that petroleum will contribute its normal share of such products.

Coumarone-indene and petroleum resins are low-priced polymers

obtained as secondary materials from the coke and petroleum industries. Their main field is in the production of cheap 'asphalt' floor tiles. Vinyl floor coverings are tending to encroach on this market.

The methacrylates are of major importance amongst the items grouped under the heading 'miscellaneous' on page 146. The usage of methacrylates in the U.S.A. expanded from 67 million lb in 1955 to 126 million lb in 1960. The basic reaction is between acetone and hydrogen cyanide to form acetone cyanohydrin.

$$\underset{\text{acetone}}{(CH_3)_2CO} + HCN \rightarrow \underset{\text{acetone cyanohydrin}}{(CH_3)_2C(OH)CN}$$

Acetone cyanohydrin reacts with concentrated sulphuric acid to form crude methacrylamide sulphate, which is reacted (without separation or purification) with methyl alcohol and water to give methyl methacrylate. The net reaction is:

$$\underset{\text{acetone cyanohydrin}}{(CH_3)_2C(OH)CN} + CH_3OH + H_2SO_4 \rightarrow \underset{\text{methyl methacrylate}}{CH_2{=}C(CH_3)COOCH_3} + NH_4HSO_4$$

Methyl methacrylate polymers are commonly encountered as clear sheets for such applications as aircraft windows. Their main shortcoming, which prevents their application to car windscreens, for example, is a relatively poor resistance to scratching and abrasion.

Polyester resins (by which is normally understood unsaturated polyester resins) and epoxy resins have also developed phenomenally, as can be seen from the U.S. consumption figures:

	1947	*1954*	*1960*
		(Million lb)	
Polyester resins	4	30	190
Epoxy resins	—	22	66

In the United Kingdom polyester resins have developed from a consumption of a few hundred tons in 1954 to 8,400 tons in 1960, and epoxy resins show a comparable scale of expansion. Polyester resins are largely used in conjunction with glass fibre, to produce the 'reinforced plastics' used in the manufacture of boats and other transport equipment. Epoxy resins are also used in conjunction with glass fibre, but in this case the end product is more commonly in the form of specialized engineering 'tools' for the mass production of pressed steel units for car bodies and aircraft parts. Epoxy resins are also of interest in the development of specialized surface coatings with an

exceptional resistance to corrosion and impact, and for the protection of electronic assemblies.

Whilst nylon is of prime concern to the synthetic fibre industry, quite a significant amount (estimated to reach 33 million lb in the U.S.A. in 1961) finds its way into the plastics field. This is normally used in small bearings, hinges, etc., where advantage may be taken of the fact that lubrication is rarely necessary.

Polyurethanes have exhibited one of the most explosive developments of the later 1950's. Originating in Germany, they have undergone spectacular commercial development in the U.S.A., illustrated by the following consumption figures (expressed in millions of lb).

	Polyurethane foams	*Polyurethane elastomers*
1956	8·5	—
1957	17	—
1958	45	0·25
1959	75	2·2
1960	110	6·7
*1961**	125	10
*1965**	325	40

* Predictions

There is also a small but rapidly expanding demand for polyurethane coatings. The main development of polyurethane resins so far has been for the production of flexible foams, in which the polyurethanes have the advantage over rubber latex of being lighter in weight and easier to process. For the future great hopes are held for the rigid foams, as a lightweight but durable insulating material for construction work.

Polyester resins, epoxy resins, nylon and polyurethanes have one factor in common, apart from their rapid industrial growth; they all draw very largely upon petroleum chemicals for their basic raw materials. As an illustration one may quote typical raw materials as follows:

Polyester resins	Ethylene glycol, propylene glycol, maleic anhydride (from benzene).
Epoxy resins	Epichlorohydrin (from propylene), diphenylolpropane (from phenol and acetone).

Nylon	Adipic acid (from benzene or cyclohexane), hexamethylenediamine (from butadiene or adipic acid), caprolactam (from cyclohexane, phenol or toluene).
Polyurethane resins	Tolylene diisocyanate (from toluene), polyethers (e.g. from propylene oxide and glycerine).

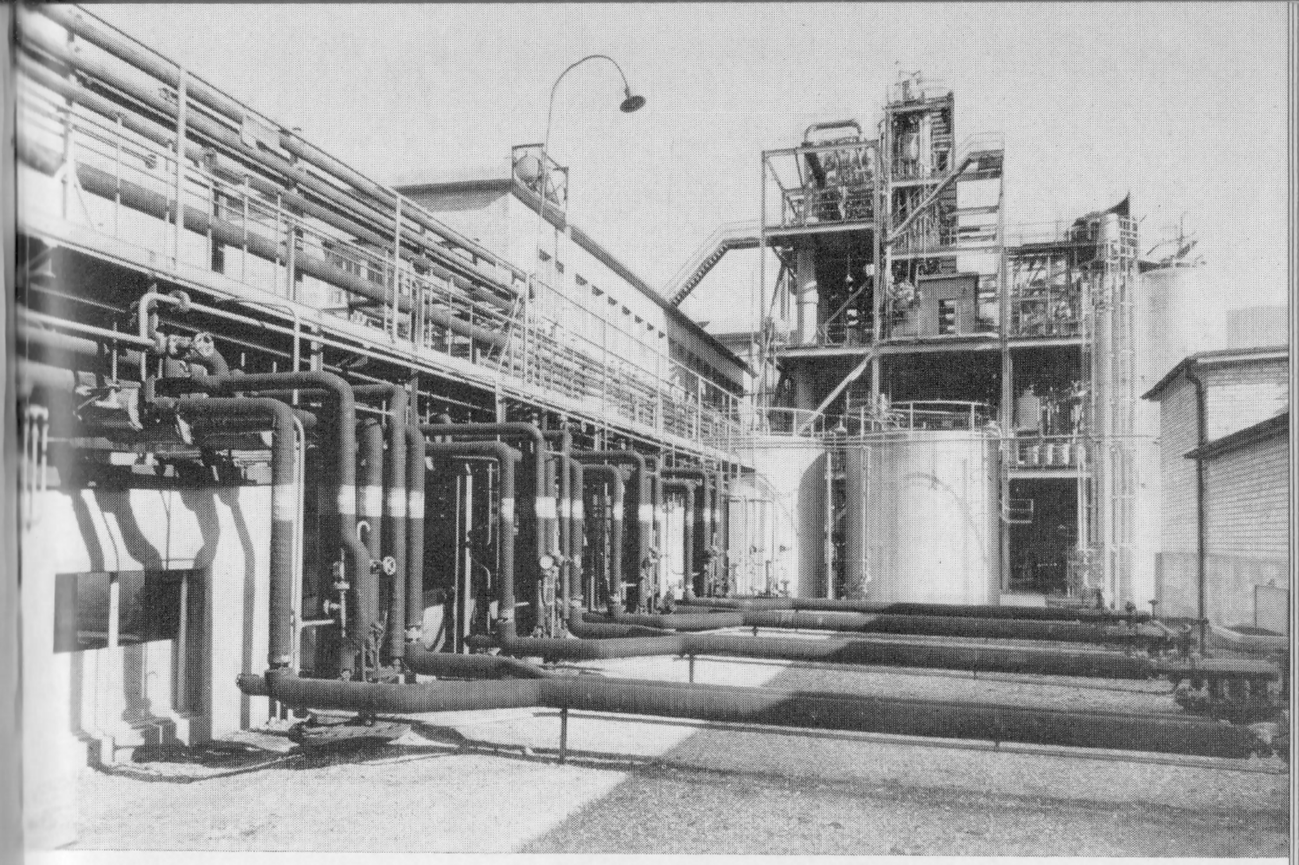
Having surveyed the developments of the 1950's, one may turn to those pending today and attempt to look a little way into the future —though any prediction must clearly be treated with some reserve. There is little doubt that many new products will enter the high polymer field, some of them modifications of an existing range, but some of them probably quite new.

Amongst the products of promise are the polycarbonates. The general equation for the production of the monomer is that between an alcohol and phosgene:

$$2ROH + COCl_2 \rightarrow R_2CO_3 + 2HCl$$

The most favoured reactant is the polyphenol diphenylolpropane, already of significance as a raw material for epoxy resins. By treating diphenylolpropane with phosgene in the presence of sodium hydroxide or an organic base, a polycarbonate is formed. Commercial production on this basis commenced in the U.S.A. in 1960, and small-scale production has proceeded for some time in West Germany. Current capacity in the U.S.A. is of the order of 10,000 tons per annum. An important characteristic of polycarbonates is that although they are thermoplastics, they have a resistance to heat which compares favourably with many thermosetting resins. The electrical properties are also claimed to be good. Polycarbonates are expected to find applications in plastic mouldings and in the form of film.

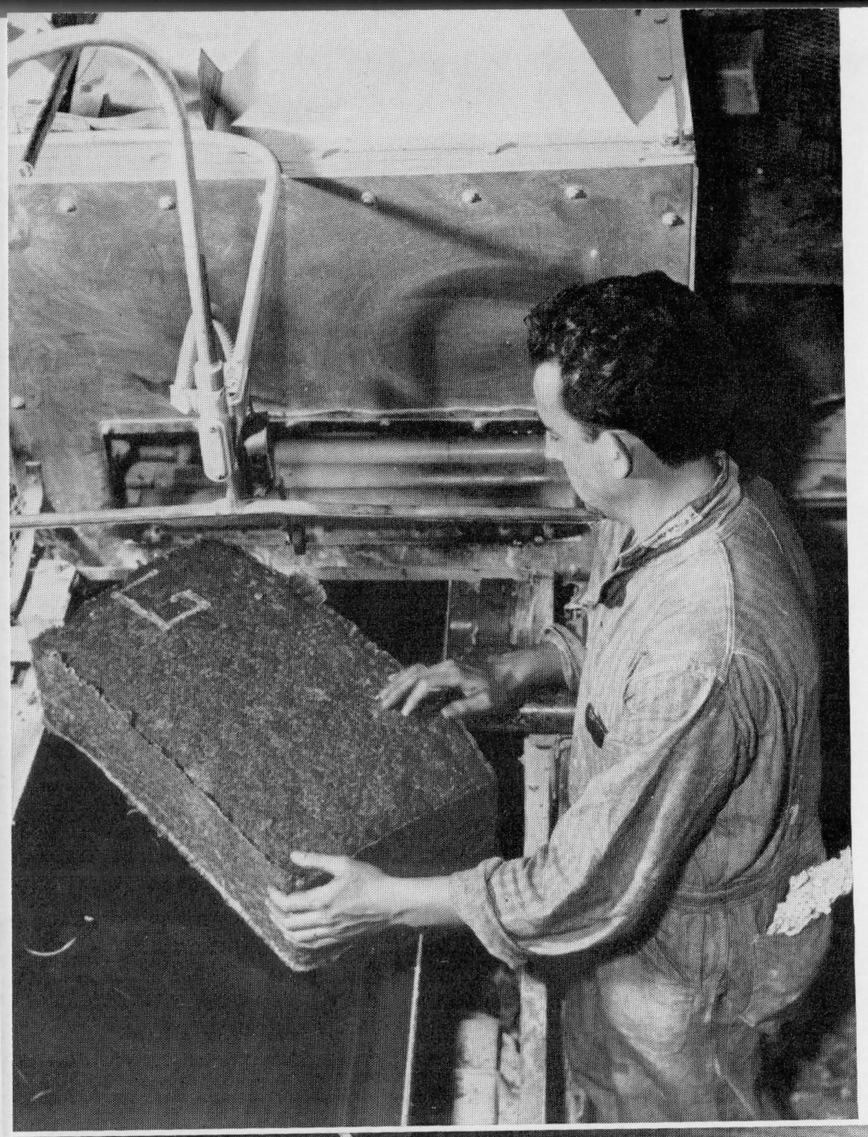
Another group of resins which is receiving much attention is the polyformaldehyde group. The technique of production has not been fully revealed, but one manufacturer bases his process on trioxane, a formaldehyde trimer. The polyformaldehydes are resins suitable for construction and engineering uses. It has been claimed that their strength approaches that of metals, so that it is expected that they could replace brass, aluminium or zinc in certain applications. A



Caprolactam plant in Switzerland

Courtesy Emse Werke A.-G.

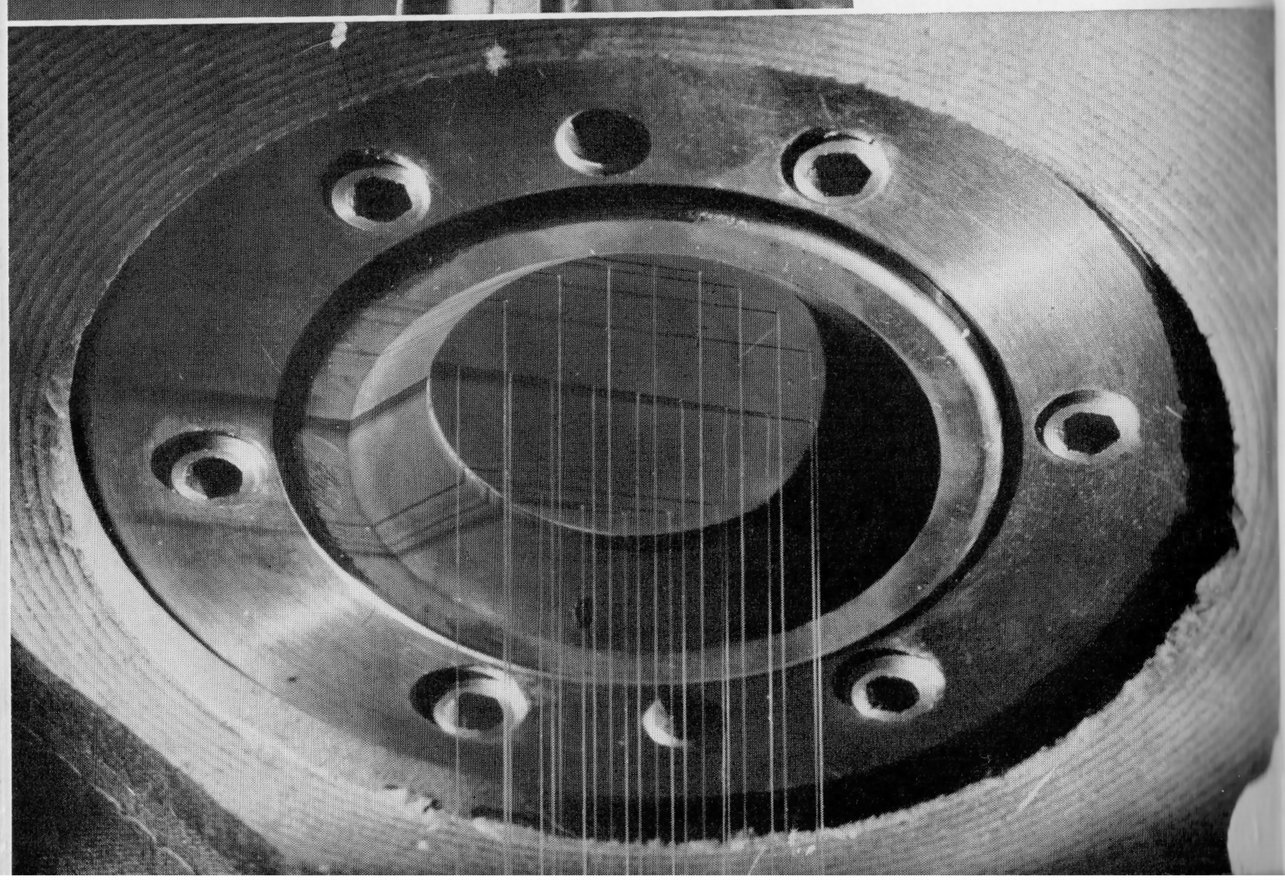
Polyolefins, from 'nibs' to finished product



A bale of synthetic rubber emerging from the press

Molten terylene fibre emerging from a spinneret

Courtesy ICI Ltd



recent assessment suggested that in the U.S.A. demand for polyformaldehyde resins could reach 70 million lb per year by 1965. The capacity in the U S.A. is about 55 million lb per year already.

On a much more limited scale, polyethylene oxide (or polyoxyethylene) resins also offer some scope for the future. The commercial resins are water-soluble, and have a marked thickening power. They have possibilities as textile processing agents, adhesives, and in cosmetic and pharmaceutical preparations. The present scale of production is still very small.

In thinking of the future of plastics, one cannot ignore the implications of techniques in current use. Reference has been made (in the cases of polypropylene and polybutadiene, for example) to the use of Ziegler-type catalysts, comprising essentially aluminium alkyls, to provide polymers of a stereo-specific nature. By this is meant that from an appropriate monomer we can prepare a polymer of predetermined regular molecular configuration. Knowledge of the influence of molecular configuration on the physical and chemical properties of polymers is not yet at a stage where we can fully appreciate or develop the implications of this possibility. There is little doubt, however, that we are on the threshold of further important industrial developments of this type.

On a global basis, the growth of the plastics industry has been one of the outstanding industrial achievements of the past decade. The growth rate for plastics has been faster than that of the chemical industry, which itself has been faster than that of the general world economy. The maintenance, in the future, of a growth rate comparable with that of the past few years, depends on the application of plastics to new fields. Two fields appear to offer significant scope for such a development. One of these lies in the increased sophistication of packaging techniques, associated with a rise in the standard of living. Another, and potentially much greater prospect, is in the broad field of construction, embracing housing, transport and industrial equipment. A relatively modest replacement of traditional constructional materials (such as metals, glass or timber) by plastics would give a tremendous impetus to the plastics industry.

Whatever the individual prospects for specific resins, there seems little doubt that there will be a further major expansion in the production and use of plastics (and hence of petroleum chemicals) in the next decade. Moreover, it is those products most closely associated

with a petroleum derivation which are proving the pacemakers in this field.

Synthetic Fibres

It has become customary to regard the term 'man-made fibres' as including derivatives of natural products (essentially the cellulose-based artificial fibres), as well as the wholly synthetic products, whereas the latter are described as 'synthetic fibres'.

Synthetic fibre production in the U.S.A. in 1960 totalled about 675 million lb (excluding 179 million lb of glass fibre). The comparable estimate for 1961 is 750 million lb (excluding 190 million lb of glass fibre). Of the 1961 total, 420 million lb are attributed to nylon, 170 million lb to acrylics, and 115 million lb to polyesters. The remaining 45 million lb includes vinyl copolymers, polyolefin fibres, etc.

In the United Kingdom 67 million lb of nylon were produced in 1960, and about 40 million lb of polyester fibres. French synthetic fibre production amounted to 72 million lb in 1959, of which 47 million lb were nylon and 20 million lb polyester fibre. The Italian production figures for 1959 totalled 51 million lb of synthetic fibres, including 43 million lb of nylon.

These figures are thrown into sharp historical perspective by reference to the fact that in 1945 the total *world* production of nylon was 24 million lb. As recently as 1951, the total world production of all synthetic fibres other than nylon (and glass fibre) amounted to 33 million lb.

It is apparent from these figures that, amongst the synthetic fibres, nylon is by far the most important product, and the U.S.A. by far the most important market.

There are important subdivisions within the nylon category, as has already been the subject of passing reference. The most significant product is nylon 66, but there is increasing competition from nylon 6. Indeed, in Europe, of the total nylon capacity, amounting to 300 million lb per year, more than half is nylon 6. Estimates for the U.S.A. suggest that, by 1965, out of a total nylon production of 680 million lb, 450 million lb will be nylon 66, and the bulk of the remainder nylon 6.

It has already been indicated that nylon 66 is derived from adipic

acid and hexamethylenediamine. Most, but not all, of this production is petroleum-based. Adipic acid, for example, can be produced from cyclohexane (usually petroleum-based) or from benzene (based on coal or petroleum). Hexamethylenediamine is obtained from the hydrogenation of adiponitrile. In its turn, the adiponitrile may come from adipic acid, butadiene or furfural. Grain residues, with a high pentosan content, represent the raw material for furfural.

After nylon, the polyesters are probably the next most important group of synthetic fibres on a world-wide basis. They are relatively more important than acrylic fibres in Europe, although the reverse is true of the U.S.A. This may reflect the European (or rather, British) origin of the polyester fibres. The essential basis of polyester fibres is the reaction between ethylene glycol and terephthalic acid (which is, for convenience, normally used in the form of the dimethyl ester). As has previously been indicated, ethylene glycol is a major ethylene derivative, via ethylene oxide, and terephthalic acid is normally an oxidation product of p-xylene from a refinery catalytic reformate.

Acrylic fibres consist essentially of polyacrylonitrile, and are therefore almost exclusively of petroleum origin.

The remaining fibres have, so far, been much less important in scale of production. The interest of petroleum in this range of fibres, however, is once again substantial. Polyolefin fibres are almost exclusively based on olefins from catalytic or thermal cracking, and the vinyl copolymers are derived to an important extent from ethylene dichloride.

Synthetic Rubbers

After the very necessary substitution of natural rubber by synthetic rubber in the latter years of the second world war (with most of the world's rubber plantations in the hands of the Japanese), the scale of production tended to drop. Production of synthetic rubber was again stimulated by the hostilities in Korea in the period 1950/51, and it has remained at a higher and increasing level since. This movement is due only partly to a substantial replacement of natural rubber by synthetic in the passenger tyre market, but, more fundamentally, to the fact that the production of natural rubber cannot be expanded rapidly, since it takes about seven years for new plantations to commence production. As a result, the availability of natural rubber

during the 1950's was not increasing as rapidly as the total demand for new rubber. Unstable political conditions in some of the rubber-growing areas have also tended to restrict the development of natural rubber.

In broad terms, it has been suggested that during the 10 years from 1959 to 1969 the world requirement of new rubber will rise from about 4 million long tons per annum to about 6 million. The contribution of natural rubber to this total is likely to remain roughly constant, at slightly over 2 million long tons per annum. The overall proportion of synthetic rubbers consumed may therefore increase from the present figure of about 50 per cent to approximately 66 per cent by 1969.

In the U.S.A. in 1960, a total of 1,558,000 long tons of new rubber was consumed. Of this total 69 per cent was synthetic. In West Germany 41 per cent of the 1960 rubber consumption of about 256,000 tons was synthetic. In the United Kingdom the equivalent figures were 39 per cent and 282,000 tons. The development of synthetic rubber production in the U.S.A. in recent years is illustrated by the following figures (the units are long tons):

	SBR	*Neoprene*	*Nitrile Rubber*	*Butyl Rubber*
1960	1,172,102	134,442	38,405	100,684
1959	1,134,908	124,815	43,620	83,028
1958	879,580	97,806	32,431	54,113
1951	704,529	58,907	15,333	76,475

Canada was a pioneer in synthetic rubber development and is the second largest producer (outside the Communist orbit) with a production of 152,000 tons in 1959, much of which was exported.

For the United Kingdom the following capacities have been quoted for synthetic rubber production:

SBR	90,000	tons	per	annum	at	end	1961
Nitrile rubber	9,000	,,	,,	,,	,,	,,	,,
Neoprene	20,000	,,	,,	,,	,,	,,	,,
Butyl rubber	30,000	,,	,,	,,	,,	,,	1963
Polybutadiene rubber	20,000	,,	,,	,,	,,	,,	,,

Of the major synthetic rubbers, all except Neoprene are overwhelmingly based on petroleum chemicals. Raw materials are as follows:

SBR	Butadiene, styrene
Neoprene	Acetylene, chlorine
Nitrile rubber	Butadiene, acrylonitrile
Butyl rubber	Isobutylene

The commercial position of synthetic rubbers is currently in a state of flux, with the development of the polydiene rubbers. In 1961 these products entered the production statistics of the U.S.A. for the first time. It is predicted that for 1961 a production will be recorded of about 16,000 long tons for polyisoprene, and 34,000 tons for polybutadiene.

These products are likely to go a long way towards filling the major technical gap in the present range of commercial synthetic rubbers. Since the polydiene rubbers are suitable for the complete or partial replacement of natural rubber in the heavier grades of tyre (for which SBR is not suitable) the requirement of natural rubber becomes very largely subject to commercial influences. Historically, the natural rubber market has been notable for its erratic fluctuations, but the availability of a complete range of synthetic products as standard prices should induce much greater stability. Also awaiting full commercial development is the ethylene-propylene copolymer group of rubbers, whose future is at present somewhat unpredictable. The newer rubbers are similar to the standard products (except Neoprene) in being essentially derived from petroleum raw material.

Detergents

Detergency, as we normally understand it, is associated with the phenomenon of surface activity on the part of the detergent molecules. Surface activity involves the orientation of detergent molecules in regular patterns, more particularly at surfaces and interfaces, but frequently also in aggregations within the body of the liquid, called micelles. These characteristics enable the detergent solution to exhibit phenomena such as reduced surface tension, foaming, and soil stabilization, which are normally associated with a detergent effect.

The traditional, and still the commonest, detergent is soap. Soap possesses a typical molecular structure for a surface active agent. It has a long hydrophobic (i.e. water-repelling) hydrocarbon chain, at one end of which is a hydrophilic (i.e. water-attracting) group. As a household detergent and industrial wetting agent, soap possesses

two important disadvantages: first, it forms insoluble calcium salts which are precipitated from hard water, and secondly, it is unstable in acid solutions.

The search to find products which would provide the detergent effect, without these disadvantages of soap, has proceeded over a long period. The first commercial developments of major significance were in the 1930's, when primary alkyl sulphates became available, using as a basis primary alcohols obtained by the reduction of fatty acids. During the second world war much attention was paid, particularly in Germany, to the manufacture of detergents that did not involve the consumption of fatty acids. Long chain paraffins (obtained from such sources as Fischer–Tropsch plants) formed the basis of the alkyl sulphonate detergents called Mersolates. Mersolates were abandoned shortly after 1945. Two other types of detergent became commercially significant at approximately the same time. In the United Kingdom secondary alkyl sulphates were produced from olefins prepared by wax cracking. Elsewhere, and particularly in the U.S.A. and Germany, alkyl benzene sulphonates were produced. In these the alkyl chain was originally in the form of a purified kerosene cut, and subsequently in the form of propylene tetramer or a narrow-range olefin cut. Both these categories of detergent have now achieved a substantial degree of development in a number of countries. Alkyl benzene sulphonates form the basis of most of the powder synthetic detergents, whilst many of the liquids are based on secondary alkyl sulphates.

All of these detergents ionize in solution and those mentioned are described as anionic, since the long chain anion is deemed to impart the specific properties of surface activity. The other type of ionizing detergent is described as cationic. Cationic detergents (e.g. cetylpyridinium chloride), in which the cation is the hydrophobic group, have never developed beyond the stage of being relatively small-scale industrial and laboratory specialities.

There is another category of detergent which has in recent years found a substantial market; this is the non-ionic detergent, which does not ionize in solution. The main type of non-ionic detergent is a condensation product of a number of molecules of ethylene oxide with a hydrophobic hydroxy compound such as an alkyl phenol. The condensation adds a number of ethylene ether groups, which are hydrophilic, to the hydrophobic portion of the molecule. The number

of added ethylene oxide molecules required to impart water-solubility to the condensed molecule depends upon the nature of the hydrophobic group.

The synthetic detergent industry today is based essentially on three groups: alkyl benzene sulphonates, the polyethylene oxide/alkyl phenol condensates, and the secondary alkyl sulphates. There is, of course, production of other types on a significant scale, more particularly of the primary alkyl sulphates, but the three groups mentioned are the major ones. They do not form insoluble salts with calcium, and they are much more resistant to acids than is soap. They are formulated in a variety of ways to produce the ultimate industrial and domestic products, and a relatively recent tendency to use blends of different types may be noted.

The importance of synthetic detergents in comparison with soaps are illustrated by the following tables:

UNITED KINGDOM (production in thousand long tons)

Year	*Soap Production*	*Synthetic Detergent Production*	*Total Production*	*Synthetic Detergent %*
1951	567	100	667	16·5
1955	467	234	701	33·4
1958	434	278	712	39·1
1960	440	313	753	41·6

U.S.A. (millions of lb)

Year	*Soap Production*	*Synthetic Detergent Production*	*Total Production*	*Synthetic Detergent %*
1945	3,574	150	3,724	4·04
1950	2,485	1,093	3,578	30·6
1955	1,351	2,317	3,668	63·1
1959	1,126	3,129	4,255	73·5
*1960**	1,100	3,300	4,400	75·0
1965†	940	3,760	4,700	80·0

* Approximate. † Predicted.

WESTERN EUROPE (including U.K.—production in thousand metric tons)

Year	*Soap Production*	*Synthetic Detergent Production*	*Total Production*	*Synthetic Detergent %*
1950	1,818	300	2,118	14·2
1954	1,778	500	2,228	22·4
1958	1,419	975	2,394	40·7

The statistics are slightly blurred by the fact that they refer to products 'as sold', rather than to the net weight of active ingredient. This does not permit of a proper mathematical comparison, but it is a realistic one, since the products are sold in a competitive market.

It will be seen that in the areas covered by the above statistics, the same pattern is not reproduced in each case. All the areas show the same tendency for overall consumption of detergent products (including soap) to go up. In the U.S.A., however, the decline of soap has proceeded much further than elsewhere.

As might be imagined, the impact of synthetic detergents is less evident in the undeveloped areas of the world. The share of the total soap and detergent usage taken by synthetic detergents is around 15–20 per cent in Latin America, and under 10 per cent in Africa and Asia.

An incidental factor of interest in this field, which is not without a certain irony, is that the development of synthetic detergents, in addition to its effect on the consumption of soap, also undermined the established basis for the production of glycerine. Petroleum chemicals made amends, however, by developing an alternative basis for glycerine supply in the form of processes for the production of synthetic glycerine. In some respects this has reacted to the advantage of glycerine since the economic basis of a material of wholly by-product origin is always a little suspect. Production and usage of glycerine are today higher than ever, partly assisted by the stability provided by the availability of a synthetic product.

Amongst detergent products, where soap has held undisputed sway for centuries, the synthetic detergents have made a very noteworthy impact within the brief space of approximately 15 years' active trading (and much less in many parts of the world). The three major types of synthetic detergent, and a number of the lesser types, are very largely of petroleum origin, so that this development may be claimed as another industrial sphere in which petroleum chemicals have exerted an impressive influence.

Other Industries

It is a platitude that the chemical industry is its own best customer. The major chemical companies are all substantial users of chemicals (including their own chemical raw materials) as well as producers.

It is not, however, possible to develop a satisfactory statistical basis to cover such a wide range of internal transactions.

Any industry deeply concerned in the consumption of organic chemicals must (in the light of the statistical background) be a major consumer of chemicals from petroleum. Such a definition clearly applies to such classifications as dyestuffs, drugs and pharmaceuticals, and toilet preparations.

The field of inorganic chemicals from petroleum is much more confined, as has been pointed out. Petroleum-based products touch upon many industries in the form of sulphur or sulphuric acid. Explosives frequently involve the use of nitric acid, a primary derivative of ammonia.

To study in detail the whole range of industries with an interest in the use of chemicals from petroleum would tend to become repetitious, and in some cases the link of the final product with its initial petroleum origin might become tenuous. In a very broad picture, let us indicate a few of the highlights:

(*a*) Improvements in the technology of producing and applying surface coatings have arisen from the greater use of ketone and glycol ether solvents in the place of the esters, which were frequently based on fermentation products.

(*b*) A very substantial part of the world's rubber industry is concerned with the manufacture of tyres. A substantial proportion of every tyre is represented by carbon black, which is essential to provide the reinforcement which gives the modern tyre its durability.

(*c*) In the production of synthetic ammonia, natural gas, refinery gas and fuel oil already account for the major share of the world's production. A further substantial expansion in nitrogenous fertilizer usage is inevitable if the world is to feed its increasing population. There is every evidence that most of this further expansion will rely upon petroleum sources of raw material. This factor has a particularly important bearing on the overall statistics of the industry, since petroleum-based ammonia is already the most substantial product in terms of tonnage in the petroleum chemical range.

(*d*) Scientific farming methods rely not only on fertilizers for

the stimulation of plant growth, but also upon a wide range of organic chemical pesticides to control the growth of unwanted plants and insects. This is a study in itself (but outside the scope of the present book) in which chemicals from petroleum are playing a part of increasing importance.

Chapter 17

Statistics of Petroleum Chemical Production

In presenting a brief statistical outline of petroleum chemical manufacture in various areas, it is perhaps appropriate to add a few words of caution. Such statistics commonly look very authoritative, but they contain a few traps for the unwary. Factors which may complicate the interpretation include: incomplete production figures (certain statistics may exclude production for military purposes, for example), inclusion of extraneous items (for instance, plastics statistics may relate to products as sold, including plasticizers, fillers, etc.), the difficulty of obtaining authoritative figures for materials produced largely for captive use (i.e. for further synthesis on the same site), and the problem of double counting. In the case of petroleum chemicals, one also has to contend with the basic difficulty of precise definition.

It is also relevant here to mention the pitfalls offered by the various units in which statistics are presented. In the United Kingdom we are accustomed to production statistics in long tons, and imperial gallons. Statistics from the U.S.A. are more often quoted in short tons (i.e. of 2,000 lb each) and U.S. gallons (approximately five-sixths of an imperial gallon). Continental European countries use the metric ton (of 2,204 lb or 1,000 kgm). It is not uncommon for statistics to leave the precise nature of the units undefined. This book normally uses the British units, but also includes other units where specified.

The seeker after minor discrepancies in statistical information will, almost certainly, find a few to shake his head over. This is inevitable (unless the author is to 'edit' the figures) in a field so large, so broadly based, so rapid in development and so complex in integration as the one which is the subject of this book. Figures of production and consumption are taken from appropriate authorities

(including the U.S. Tariff Commission, U.K. Board of Trade Statistics, and the estimates put forward by major journals). They may therefore be treated as informed judgements, rather than as precisely factual information.

The tables of production figures which follow illustrate the importance of petroleum chemicals within the chemical industry. In passing, we should make some reference to the significance of this production in terms of the petroleum industry. This is of some importance if one bears in mind the frequently reiterated (and so far unjustified) fears of the imminence of the depletion of this planet's petroleum resources. The net usage of petroleum products as raw materials in the production of petroleum chemicals represents 2–3 per cent of the production of petroleum and natural gas in the non-Communist world as a whole. This percentage is tending to increase, but only slowly, since the production of petroleum itself is also increasing at a substantial rate. It can be seen, therefore, that the contribution of petroleum chemicals towards the depletion of petroleum resources is relatively very slight.

PRODUCTION FIGURES FOR THE U.S.A. (in thousand million lb per year)

	Total Chemicals Produced	*Total Petroleum Chemicals Produced*	*% Petroleum Chemicals*
1935	20	1	5
1940	25	2·5	10
1945	65	10	15
1950	75	15	20
1955	120	30	25
1960	170	55	32

Further predictions suggested that the percentage of petroleum chemicals would reach 40 in 1965 and 50 in 1970. In round figures, the 55,000 million lb production for 1960 included 35,000 million lb aliphatic organic chemicals, 5,000 million lb aromatic organic chemicals, and 15,000 million lb inorganic chemicals.

These figures include a certain amount of double counting (i.e. where isopropyl alcohol is used to make acetone which is used to make diacetone alcohol which is used to make methyl isobutyl ketone, the total production of each is added together). A picture of the organic chemical position in the U.S.A. with double counting eliminated as far as possible is as follows:

	Total Organic Chemicals	*Organic Chemicals from Petroleum*	*% Organic Chemicals from Petroleum*
1950	—	—	57
1955	—	—	74
1959	11·25 million metric tons	9·4 million metric tons	84
1960	11·75 „ „ „	9·9 „ „ „	85

PRODUCTION FIGURES FOR CANADA

In 1961, petroleum chemicals in Canada, expressed in terms of output value, represented over 18 per cent of the total chemical industry.

Excluding sulphur, the tonnage of petroleum chemicals was put at 625,000 long tons in 1959, rising to perhaps 1,100,000 long tons by 1965. The inclusion of sulphur would, in this case, tend to distort the tonnage picture, since it is frequently predicted that Canadian sulphur recovery may amount to about two million long tons in 1965.

PRODUCTION FIGURES FOR THE UNITED KINGDOM

Organic Chemicals from all Sources (in thousand metric tons)

	1949	*1953*	*1955*	*1962*
Coal tar	175	230	275	540
Acetylene	70	80	110	150
Synthesis gas	55	70	80	90
Fermentation	160	170	140	130
Petroleum	30	200	290	1,500
	490	750	895	2,310
Proportion from petroleum	6%	27%	32%	65%
Investment ($ million equivalent, at year end)	—	—	125	553
Inorganics from petroleum (thousand metric tons)	15*	60	90	300

* 1950.

Another source gives the following figures of production (in millions of long tons); once again an effort has been made to eliminate double counting.

	Total Organic Chemicals	*Organic Chemicals from Petroleum*	*% Organic Chemicals from Petroleum*
1955	—	—	31
1959	1·3	0·55	42
1960	1·42	0·70	49

PRODUCTION FIGURES FOR WESTERN EUROPE

One estimate of the total organic chemical production in Western Europe (including the United Kingdom) in 1959 is 5·5 million metric tons, of which 1·7 million metric tons, or 31 per cent, was derived from petroleum.

Another assessment is as follows (production in millions of metric tons):

	Total Organic Chemicals	*Organic Chemicals from Petroleum*	*% Organic Chemicals from Petroleum*
1955	—	—	19
1959	5·45	1·6	29
1960	6·0	2·2	37

Production of petroleum chemicals in the individual countries of Western Europe (in thousands of long tons of finished products) is shown in the following Table:

	ORGANIC CHEMICALS						INORGANIC CHEMICALS
	U.K.	*West Germany*	*France*	*Nether-lands*	*Italy*	*Total*	*Western Europe*
1950	48	62	1	4	1	116	7
1952	148	92	13	5	18	276	52
1954	256	135	47	18	36	492	230
1956	339	228	90	38	72	767	542
1958	474	383	152	55	137	1,201	1,212

These figures largely speak for themselves. The U.S.A. still leads the field with a petroleum chemical production nearly six times as great as that of the whole of Western Europe. The difference is narrowing, since the rate of expansion in Europe is now higher than in the U.S.A. It is clear that in the organic chemical field, products of petroleum origin, having taken 85 per cent of the total U.S.A.

market, cannot expand much more rapidly than organic chemicals as a whole.

The production of inorganic chemicals from petroleum, while very substantial in absolute terms, is still quite a minor factor in the total inorganic chemical picture. This situation will continue, for reasons outlined at the beginning of this book.

It should perhaps be indicated that the rate of growth within the chemical industry is by no means uniform. In the United Kingdom, heavy organic chemicals have been expanding at the rate of about 10 per cent per annum, whereas the growth rate for basic inorganic chemicals has been about half this figure. This difference is likely to be maintained, since it is the dynamic industries such as plastics, synthetic rubbers and synthetic fibres that are setting the pace for organic chemicals. The production of chemicals from petroleum has been expanding in the U.K. in recent years at the rate of nearly 20 per cent per annum. Such an exceptionally high figure can hardly continue for very many more years, for it would involve a cumulative increase in production and investment that would become increasingly difficult to maintain.

The rate of growth of the group of industries under the category of Chemical and Allied Industries in the United Kingdom is of the order of 6 per cent per annum. When this is seen in relation to the growth rate for the United Kingdom economy as a whole, which has been about 3 per cent during a decade which may reasonably be regarded as prosperous, the performance of the chemical industry as a whole, and particularly that segment of it using petroleum as a raw material, has been outstanding.

Bibliographical Note

Books on petroleum chemicals have never been numerous. Three, published fairly recently, are as follows:

Goldstein: THE PETROLEUM CHEMICAL INDUSTRY (*2nd ed. 1958*); E. & F. N. Spon, London.

Astle: THE CHEMISTRY OF PETROCHEMICALS (*1956*); Reinhold Publishing Corp., New York.

Steiner (ed.): INTRODUCTION TO PETROLEUM CHEMICALS (*1961*); Pergamon Press, London.

The third of these is a collection of papers presented at a symposium, and is not therefore an attempt at a comprehensive survey of the whole subject.

To this list one should add:

Faith, Keyes & Clark: INDUSTRIAL CHEMICALS (*2nd ed. 1957*); Chapman & Hall, London.

This book is by no means limited to petroleum chemicals, but it is a treasury of information on the industrial aspects of a long list of chemical products, with particular reference to the U.S.A.

Dealing with more specialized aspects of industrial activity associated with petroleum chemical products, there is a variety far too great to be listed here. A typical selection, embracing topics of major interest to the petroleum chemical field, could include the following:

Schwartz, Perry & Berch: SURFACE ACTIVE AGENTS AND DETERGENTS (Vol. II) (*1958*); Interscience Publishers, New York.

Moilliet, Collie & Black: SURFACE ACTIVITY (*2nd ed. 1961*); E. & F. N. Spon, London.

Whitby (*ed.*): SYNTHETIC RUBBER (*1954*); John Wiley, New York.

Moncrieff: MAN-MADE FIBRES (*3rd ed. 1957*); National Trade Press, London.

Simonds: CONCISE GUIDE TO PLASTICS (*1957*); Reinhold Publishing Corp., New York.

Curme & Johnston: GLYCOLS (*1953*); Reinhold Publishing Corp., New York.

Miner & Dalton: GLYCEROL (*1953*); Reinhold Publishing Corp., New York.
Doolittle: TECHNOLOGY OF SOLVENTS AND PLASTICISERS (*1954*); John Wiley, New York.
de Ong: CHEMISTRY AND USES OF PESTICIDES (*2nd ed. 1956*); Reinhold Publishing Corp., New York.
Paisley: FERTILISERS AND MANURES (*1960*); Collingridge Ltd., London.

A constant source of new information on petroleum chemicals is to be found in a number of journals. Notable chemical and chemical engineering journals in the English language include *Chemistry & Industry*, *Chemical Age*, *Chemical Week*, *Chemical & Engineering News*, *Chemical Engineering*, and *Chemical Engineering Progress*. Such journals include, *inter alia*, the news of new developments in the petroleum chemical field, as well as occasional feature articles covering various aspects of the subject. Much of the statistical information included in the text has been drawn from such sources.

Three specific references cover the recent position in petroleum chemicals, largely from a European point of view, and may be found of interest:

Hoog, *Chemistry & Industry*, 1961, 1374 (September 2nd).
Hodge, *Chemical Engineering Progress*, **57**, (2), 37 (February 1961).
Blanco, *Chemistry & Industry*, 1961, 802 (June 17th).

Petroleum journals also display a lively interest in the association of their industry with the production of chemicals. *Oil & Gas Journal*, for instance, publishes regular reviews of the status of production, plants, and producers in this field. *Petroleum Refiner* makes a speciality of publishing a series of process data sheets, including flowsheets and relevant process, economic, and licensing data covering petroleum and chemical processes. *Petroleum Times* includes frequent feature articles covering the chemical field.

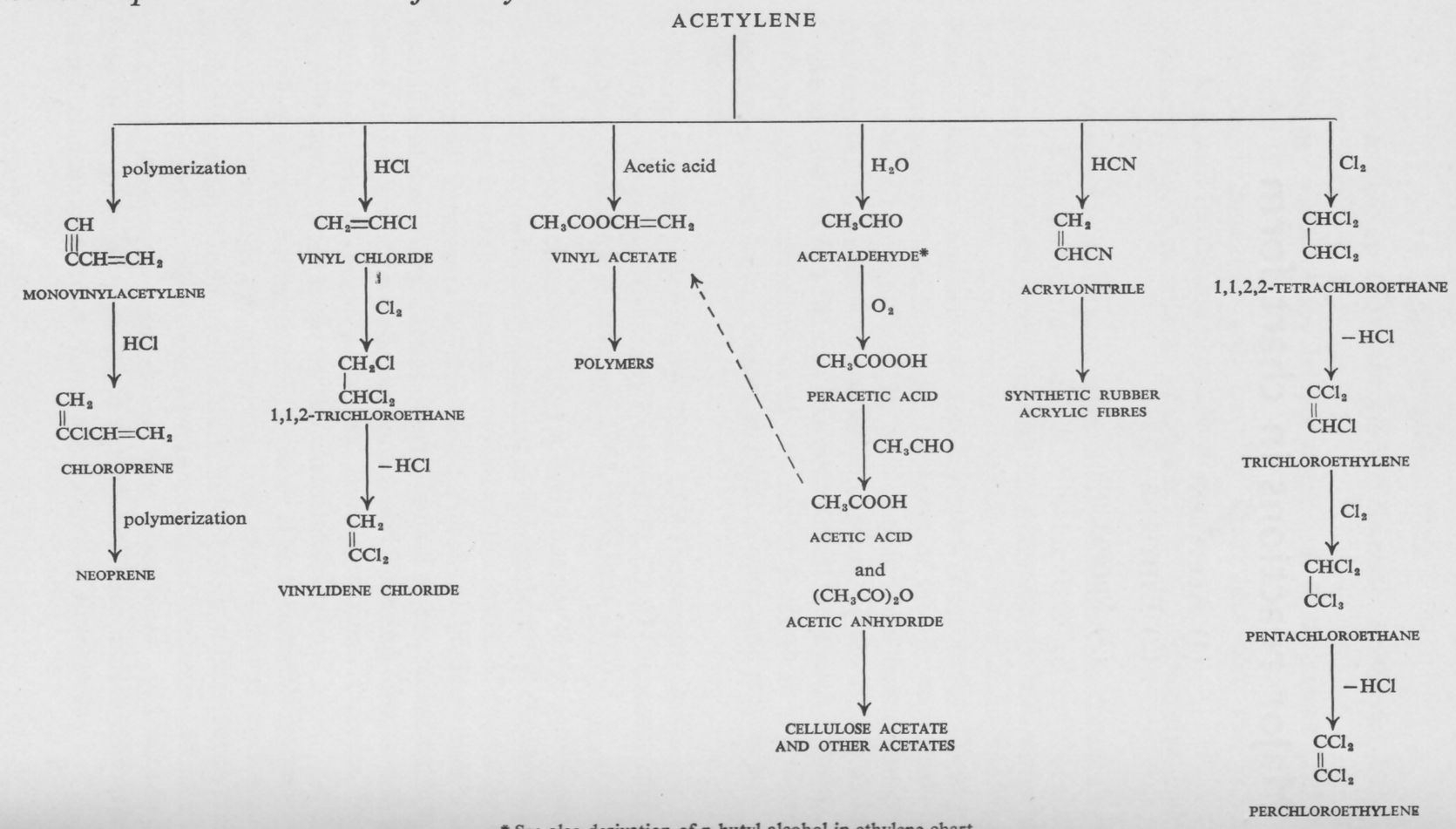
Industries with an incidental (or more than incidental) interest in petroleum chemicals are numerous, and each is served by several publications. Such industrial fields include plastics, rubber, soaps and detergents, textiles, paints and surface coatings, fertilizers and so on.

Certain economic journals include occasional well-informed features on petroleum chemical activities. These include *Financial Times*, *Economist* and the *New York Journal of Commerce*.

Major reactions in chart form

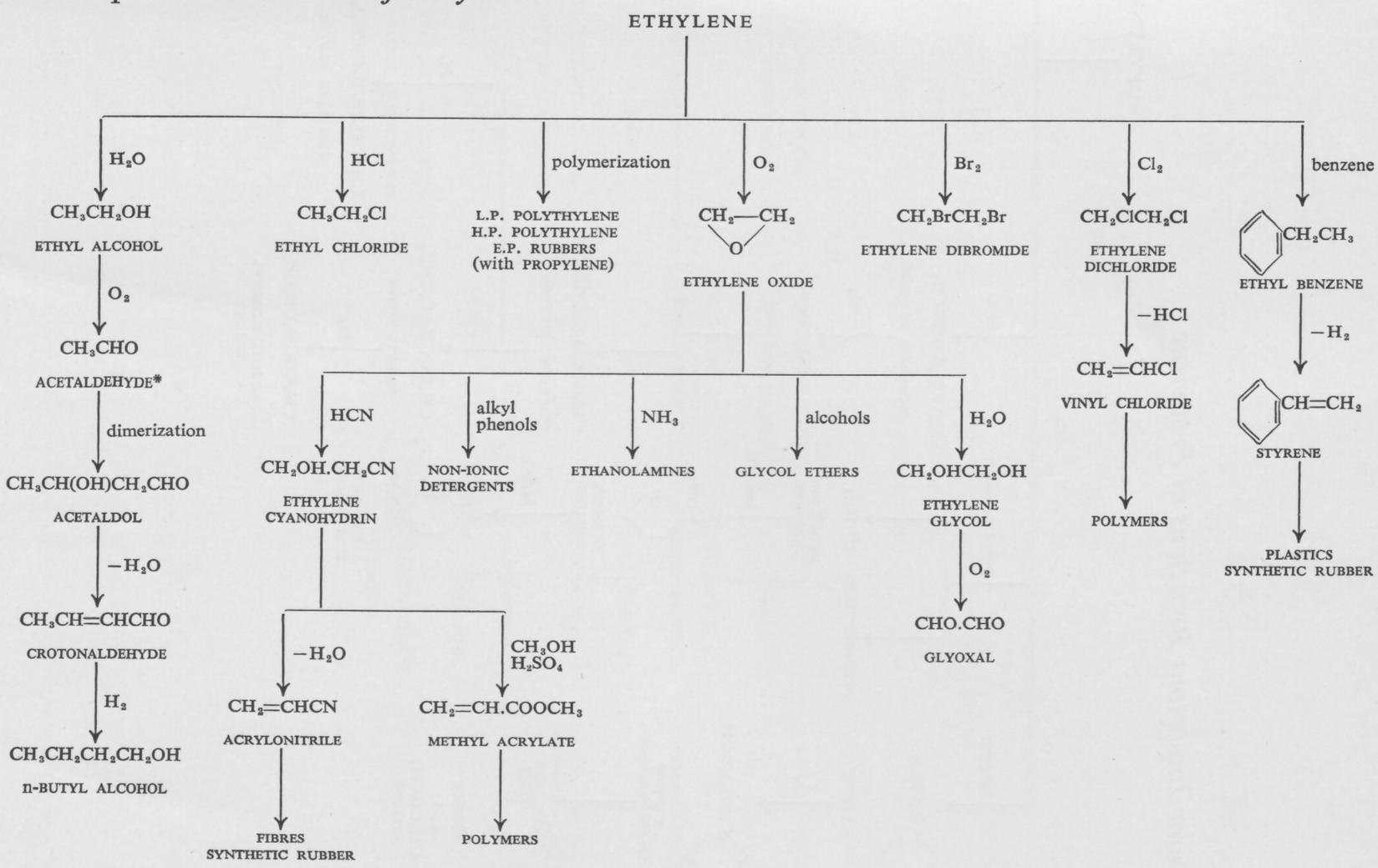
(1) ACETYLENE
(2) ETHYLENE
(3) PROPYLENE

Some Important Reactions of Acetylene



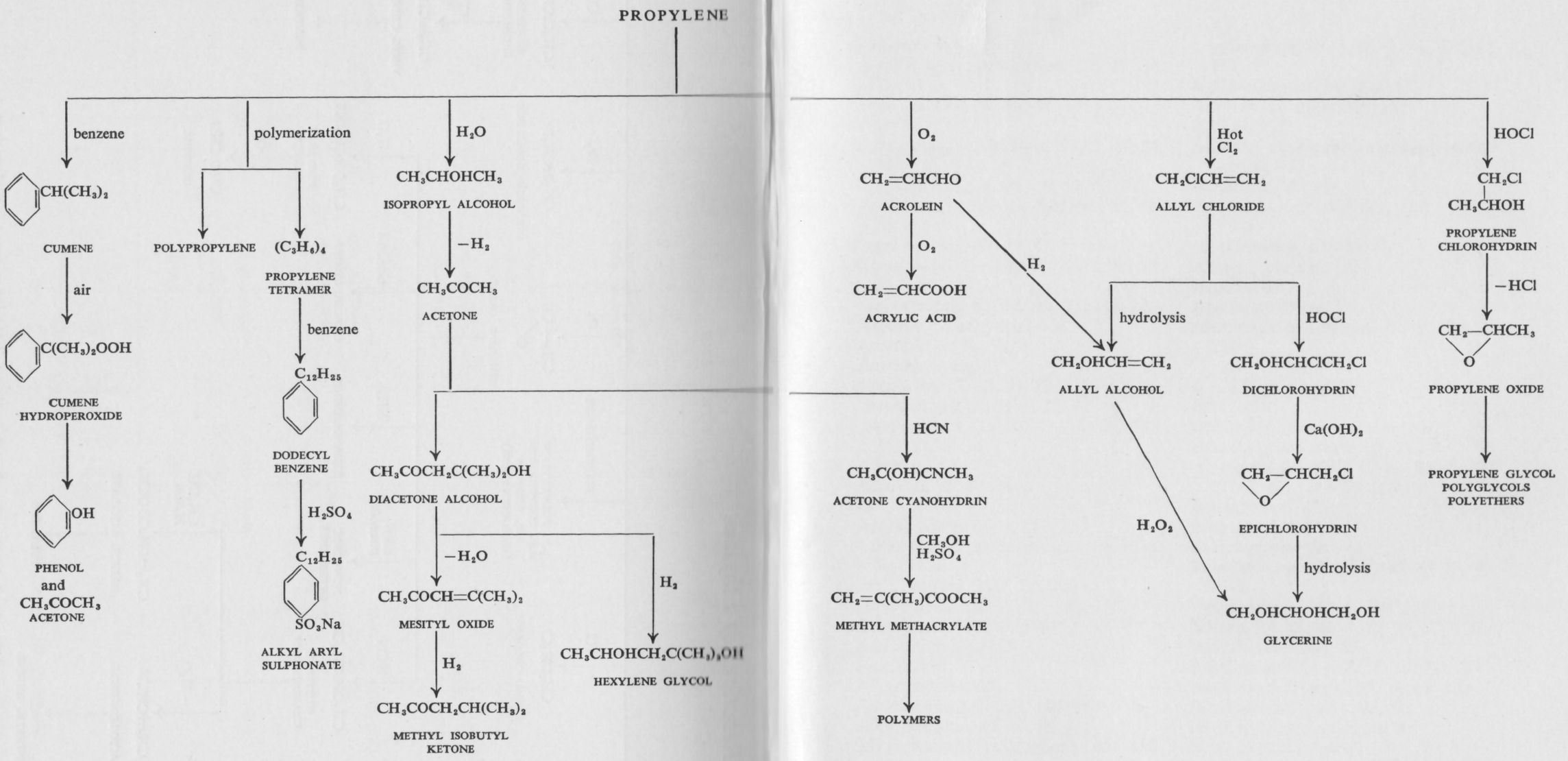
* See also derivation of n-butyl alcohol in ethylene chart.

Some Important Reactions of Ethylene



* See also derivation of acetic acid, acetic anhydride and acetates in acetylene chart.

Some Important Reactions of Propylene



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